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SCHOOL OF
DENTAL MEDICINE

Medico-Chirurgical College.



Skeleton Notes on the Lecture Course

—IN—

Organic and Clinical CHEMISTRY.



Second Year Students.

SESSION 1900-1901.

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ORGANIC CHEMISTRY.

It was a matter of early observation that, while many of the naturally occurring mineral compounds could be synthetically produced in the chemical laboratory by strictly chemical means, those compounds which, in nature, are peculiar to animal and vegetable structures, or organic remains, did not admit of preparation from their elementary constituents outside the organism. The early chemists (early part of 19th Century) consequently came to the conclusion that such compounds could not be produced except through a control of chemical processes by the "life force". The study of compounds which to them seemed peculiar to organisms was therefore called "Organic Chemistry",.

To day the term organic chemistry has a totally different significance. For to day we are able to build up gradually, by strictly chemical means, representatives of nearly all classes of organic compounds — the principal exception being that of the "albuminous bodies". But even the albuminous bodies may be made to undergo in the laboratory many chemical changes that are essentially identical with the changes they undergo in the organism. From which it will be seen that the "life force" control is not necessary to the production of "organic" compounds.

Since, however, organic compounds do, in nature, occur in organisms or in organic remains; and since the number of the organic compounds is enormous; it is convenient to study such compounds as a separate branch of chemistry under the title, "organic chemistry".

All organic compounds are alike in that they contain the element carbon — the molecules of these compounds being structures (often of exceeding complexity) of atoms built upon frameworks, or skeletons of carbon atoms. Moreover all organic compounds may be considered as derived from simple compounds of carbon with hydrogen — called HYDROCARBONS. We have thus three names by which we may designate the study of organic compounds. These names in order of merit are:

CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

CHEMISTRY OF THE CARBON COMPOUNDS.

ORGANIC CHEMISTRY.

Physiological Chemistry limits itself to a study of the normal chemical processes of the organism.

Pathological Chemistry is concerned with the study of abnormal chemical changes in the organism.

Fermentation Chemistry studies the chemical changes induced by the organized and unorganized FERMENTS. It is a department of both physiological and pathological chemistry.

Hygienic Chemistry has for its aim the application of chemistry in the prevention of disease. It draws its information from the other branches of chemistry.

Clinical Chemistry seeks to apply all pertinent facts of chemistry to the diagnosis and cure of disease.

Physiological, pathological, fermentation, hygienic and clinical chemistry are all, essentially, departments of the chemistry of the hydrocarbons and their derivatives—modern thought being opposed to the conception of a "life force" as essential to any of the chemical changes concerned.

Whereas the study of mineral, or "inorganic" chemistry must concern itself with about seventy elementary forms of matter, forming relatively few compounds, the study of organic chemistry is mainly concerned with four elements only — carbon, hydrogen, oxygen, and nitrogen — but the number of possible compounds is, according to our best knowledge, practically infinite. The necessity for organic chemistry as a separate branch is thus made evident.

E L E M E N T A R Y O R G A N I C A N A L Y S I S .

In the discussion under this head we will present, in outline only, principles of chemical analysis by means of which we may determine the percentage composition and the EMPIRICAL FORMULAE of compounds containing carbon, hydrogen, oxygen and nitrogen: and also sulphur and phosphorus.

CARBON & HYDROGEN:— These elements are determined by burning the body, at a red heat, in a "combustion tube" of glass, porcelain or platinum, with oxygen. Under such circumstances the carbon of the compound is burned to carbon dioxide, CO_2 ; and the hydrogen is burned to steam, H_2O . The gaseous products CO_2 and H_2O are aspirated through a weighed tube containing dry calcium chloride, CaCl_2 . The H_2O is absorbed by the CaCl_2 and the increase in weight of the tube is the weight of water absorbed. The CO_2 is further aspirated through a weighed tube filled with grains of a mechanical mixture of sodium hydroxide (NaOH) with lime (CaO). The CO_2 is absorbed in this tube, forming sodium carbonate, Na_2CO_3 ; and the increase in weight of the "soda lime" tube is the weight of CO_2 absorbed.

We are now in a position to calculate the percentages of carbon and hydrogen in the body under examination. We must first calculate the weights of carbon and hydrogen from the observed weights of CO_2 and H_2O , thus:

$$\text{CO}_2 : \text{C} = 44 : 12.$$

$$44 : 12 = \text{Observed weight of CO}_2 : \text{Required weight of C.}$$

$$\text{H}_2\text{O} : \text{H}_2 = 18 : 2.$$

$$18 : 2 = \text{Observed weight of H}_2\text{O} : \text{Required weight of H}_2.$$

NOW CALCULATE PERCENTAGES, THUS:

Weight of carbon determined

$$\frac{\text{Weight of body taken}}{\text{Weight of body taken}} \times 100 = \text{Per cent of carbon in body.}$$

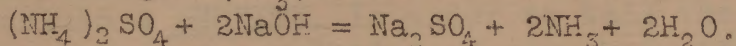
$$\frac{\text{Weight of hydrogen determined}}{\text{Weight of body taken}} \times 100 = \text{Per cent. of hydrogen in body.}$$

=====

NITROGEN:— This element is most conveniently determined by the method of Kjeldahl. The principles concerned are as follows:

I. The nitrogenous body is vigorously boiled in concentrated sulphuric acid, (H_2SO_4). This treatment so operates as to bring about the formation of ammonium sulphate $[(\text{NH}_4)_2\text{SO}_4]$, which salt contains all of the original nitrogen of the body under examination.

II. Solution I is made strongly alkaline with sodium hydroxide (NaOH) and then boiled. The ammonium sulphate is decomposed by this process, with the formation of sodium sulphate, Na_2SO_4 , and the liberation of ammonia gas (NH_3):



III. The NH_3 liberated from solution II is conducted into, and absorbed by a solution that contains a known weight of hydrochloric acid HCl —the HCl being in excess: $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$.

A portion of the HCl is thus neutralized by the NH_3 .

IV. Solution III is TITRED with a STANDARD solution of NaOH , using phenol phthalein or another efficient indicator. The excess of HCl is thus determined — from which the quantity of HCl required to neutralize the NH_3 is obtained by subtraction.

V. Calculate the HCl equivalent to nitrogen (in ammonia), thus:

$$\text{HCl} : \text{N} = 36.5 : 14.$$

$36.5 : 14 = \text{weight of HCl used to neutralize the } \text{NH}_3 : \text{Required weight of nitrogen.}$

VI. Calculate the percentage of nitrogen, thus:

$$\frac{\text{Weight of Nitrogen determined}}{\text{Weight of body taken}} \times 100 = \text{Per cent. of nitrogen in body.}$$

VOLUMETRIC ANALYSIS:— We have used the terms TITRE and STANDARD SOLUTION, in explaining Kjeldahl's method for the determination of nitrogen in organic bodies. It is necessary that the meaning of these terms should be explained.

The principle upon which volumetric analyses are based is this:— By means of the balance we prepare a solution, one unit volume of which (usually 1 c.c.) is made to contain a certain weight of some chemically active substance—the exact substance used being dependent upon the particular analysis we desire to make. Such KNOWN solution is called a STANDARD solution.

If, now, in the course of an analysis we prepare another solution that contains an unknown weight of some body that can enter into a definite chemical reaction with the body in the standard solution, the standard solution furnishes us with means for determining the actual weight of active material in the unknown solution. It is only

necessary for us to measure the number of unit volumes of the standard solution, required to conclude a certain reaction with all of the active material in the unknown solution. Then, since each unit volume of the standard solution corresponds or is equivalent to a definite weight of the active body in the unknown solution, it is simply necessary to multiply the number of unit volumes of standard solution used, by the previously determined factor which expresses the weight of active material in the unknown solution equivalent to one unit volume of the known or standard solution.

We are therefore required to have some means both for measuring the volume of standard solution used; and for determining when the reaction has been fully completed. In order to measure the volume of standard solution employed, we make use of a narrow, graduated glass cylinder, called a BURETTE. In order to tell the end point of our TITRATION we make use of a solution of some body that is capable of giving a marked color change with a minute quantity of our standard solution, but cannot do so as long as any of the active material in the unknown solution remains unacted upon. Such a body is termed an INDICATOR -- because it indicates the completion of the principal reaction.

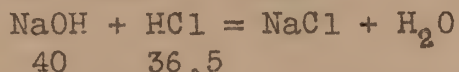
Passing from the above general exposition of the nature of volumetric analyses; and coming to the Kjeldahl method for the determination of nitrogen: we have to consider the quantitative relations of the reaction between NH_3 and HCl . The reaction is written



Therefore 14 parts of nitrogen correspond to
 36.5 parts of hydrochloric acid.

In the course of our analyses we obtained a solution that contained all of our nitrogen as ammonia. This would be our unknown solution -- for, while we know that it contains all of our nitrogen as ammonia, we do not know the weight present.

Let us now have prepared two standard solutions -- one containing 3.65 grams of HCl per litre (= .00365 grams per c.c.); and the other containing 4 grams of NaOH per litre (= .004 grams per c.c.). Any given volume of either of these solutions would be exactly equivalent to the same volume of the other -- Thus:



Suppose that the body being analyzed weighed 5 grams and that its nitrogen after being changed to ammonia was distilled into 50 c.c. of our standard HCl . Some of the HCl would have been changed to neutral NH_4Cl . Now add a few drops of an alcoholic solution of phenol-phthalein (which is colorless in the presence of free HCl ; but is crimson in the presence of free NaOH); and then run into the solution, from a burette, NaOH solution until a red color appears. Suppose that 30 c.c.

NaOH solution accomplished this result. Evidantly $50 - 30 = 20$ c.c. of our HCl was neutralized by the unknown weight of NH_3 . But 1 c.c. HCl we know to be equivalent to .0014 grams of nitrogen. Therefore our 5 grams of sample contained $.0014 \times 20 = .028$ grams of nitrogen. The percentage of nitrogen is therefore $\frac{.028}{5} \times 100 = .56$

NOTE: By means of special volumetric analyses we determine clinically the quantitative composition of urines, gastric juice &c.

DETERMINATION OF SULPHUR AND PHOSPHORUS :—

In order to determine the percentage of sulphur and phosphorus in organic bodies we heat the bodies with strong nitric acid. By this treatment the sulphur is converted to sulphuric acid and phosphorus to orthophosphoric acid. These are precipitated separately (the sulphuric acid by barium chloride in the presence of hydrochloric acid: and the phosphoric acid by magnesium chloride in the presence of ammonium hydroxide). and weighed, after ignition in a platinum crucible, as barium sulphate (BaSO_4), and magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), respectively. The weight of BaSO_4 and $\text{Mg}_2\text{P}_2\text{O}_7$ are calculated to S and P_2 respectively; and thence the percentages of sulphur and phosphorus in the organic body are obtained.

DETERMINATION OF OXYGEN:— Oxygen being difficult to determine directly, is usually determined by difference. We determine all the other elements in the body, and subtract the sum of the percentages from 100. The remainder is taken as being the percentage of oxygen.

CALCULATING EMPIRICAL FORMULAE.

Having obtained the percentages of the various elements that enter into the composition of the organic body under examination we are in a position to calculate its empirical formula.

By the empirical formula for a body we mean the simplest formula that shows a composition in harmony with our elementary analysis.

The method for calculating empirical formulae will be understood from an inspection of the subjoined example. An elementary analysis of lactic acid showed that it has the following elementary composition:

Carbon = 40.00 per cent.

Hydrogen = 6.6 per cent.

Oxygen = 53.40 per cent.

100.00 per cent.

Divide the above numbers by the respective atomic weights:

$$\begin{array}{r} \frac{40}{12} = 3.3 \qquad \frac{6.6}{1} = 6.6 \qquad \frac{53.4}{16} = 3.3 \\ 3.3 : 6.6 : 3.3 = \\ 1 : 2 : 1 \end{array}$$

The carbon and oxygen atoms are therefore equally numerous in lactic acid; but the hydrogen atoms are twice as numerous as either the carbon atoms or the oxygen atoms. The simplest formula for lactic acid

is therefore CH_2O .

UNSATISFACTORY NATURE OF EMPIRICAL FORMULAE.

We have seen above that the formula CH_2O expresses an elementary composition in entire accordance with our analytical knowledge concerning lactic acid. But that this formula is quite irrational is evidenced by the fact that we know a number of bodies that have properties widely differing from the properties of lactic acid; but to which we would give an identical empirical formula. Such bodies are formaldehyde, formose, grape sugar, fruit sugar, acetic acid, &c., &c.

A rational formula for lactic acid would show the manner in which lactic acid differs from the other bodies mentioned. Now the formula for lactic acid may very well be some MULTIPLE of CH_2O . We must therefore, in the light of our now knowledge, write $(\text{CH}_2\text{O})_n$ as the formula for lactic acid. The n meaning some definite whole number as yet undetermined. We are, therefore, at this stage of our studies, entirely unacquainted with the true molecular weight of lactic acid; and have no means for explaining why its properties should be expected to differ from those of certain other bodies having an identical percentage composition.

DETERMINATION OF TRUE MOLECULAR WEIGHT.

We have a number of methods by means of which we may arrive at conclusions as to the molecular weights of bodies. Two of these methods we will now discuss.

MOLECULAR WEIGHT BY CHEMICAL REASONINGS:—Let us consider the well known compound, water — seeking to discover how many times heavier is its molecule than an atom of hydrogen.

From our analyses of water we know it to be composed of hydrogen, one part; and oxygen eight parts by weight. Each molecule of water therefore contains at least one atom of hydrogen and one atom of oxygen. We might for the moment, write the formula HO (which would make oxygen have an atomic weight of 8.)

Now 23 parts of the element sodium can react with 18 parts of water, liberating 1 part of hydrogen; and forming a perfectly definite compound that contains all of the sodium that was used, all of the oxygen from the water, and $1/2$ of the hydrogen from the water. It is a primary conception that an atom cannot be divided; and, since we have observed that the hydrogen in the water molecule can be split into two equal parts, it is an unavoidable conclusion that the molecule of water must contain AT LEAST two atoms of hydrogen. We are consequently in a position to write the formula, H_2O , for the molecule of water.

No experiment has ever shown that the hydrogen in the water molecule can be divided into more than two parts. Also, no one has ever been able to divide the oxygen in the water molecule. We have, then (since many experiments and more experimenters have examined water) most excellent reasons for writing the formula H_2O as truly expressing

Page 7.

the molecule of water. But the atom of hydrogen is taken as unity — the hydrogen in the water molecule therefore weighs two; and, since we know by analysis that water has eight times as much oxygen as hydrogen it follows that the oxygen in the water molecule must weigh ($2 \times 8 = 16$) sixteen. The molecular weight of water is therefore ($2 + 16 = 18$) eighteen: or, in other words, the molecule of water weighs eighteen times as much as one atom of hydrogen.

By similar reasonings we could come to the conclusion that the molecule of hydrochloric acid contains one atom of hydrogen. We know by analysis that one part by weight of hydrogen in hydrochloric acid can be displaced by 107.7 parts by weight of silver, with the production of silver chloride. Therefore 107.7 parts by weight of silver (which has been set as the atomic weight of silver) is equivalent to one "acid" hydrogen atom.

It is quite easy for us to prepare silver lactate and to analyze the salt. We find that the same weight of silver (107.7) as is equivalent to one molecule of hydrochloric acid (36.5) is also equivalent to 90 parts of lactic acid. Lactic acid therefore contains one "acid" hydrogen atom and has a molecular weight of 90.

The formula CH_2O , however, gives us a molecular weight ($12 + 2 + 16 = 30$) of 30. We must therefore ($30 \times 3 = 90$) triple our formula CH_2O and write the formula for lactic acid $(\text{CH}_2\text{O})_3$. We have thus found our previously unknown "n" to be 3.

We know, nevertheless, that the body trioxymethylene has the formula $(\text{CH}_2\text{O})_3$ (i.e. it is identical with lactic acid in elementary composition and molecular weight); and we are, consequently, still without means for saying why we should expect the two bodies to be so very different in their properties — as we know them to be. When we come to study the structures of the respective molecules we will be furnished with our desired explanation.

We will now consider another example. Ethane is a well known gas. Analysis shows it to have the following composition:

Carbon = 4 parts.

Hydrogen = 1 part.

Calculate the empirical formula

$$\frac{4}{12} = \frac{1}{3} \qquad \frac{1}{11} = 1.$$

The hydrogen atoms are thus three times as numerous as the carbon atoms in the molecule of ethane. We thus arrive at the empirical formula: $(\text{CH}_3)_2$.

But we find that 1/6 of the hydrogen in the ethane molecule may be replaced by chlorine, with the production of the definite body, ethyl chloride. The ethane molecule must therefore contain at least six hydrogen atoms and the formula must be C_2H_6 — i.e., "n" here is

MOLECULAR WEIGHT BY AVOGADRO'S LAW:— The famous law of the Italian physicist, Avogadro, may be stated thus: "Equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules". It, obviously, follows at once, from this law, that the relative weights of the molecules of the various gases, are proportional to the relative densities of the gases.

It is therefore, in fixing molecular weights by the application of Avogadro's law, first necessary to fix the molecular weight of hydrogen (the hydrogen atom being the unit of mass); and then to determine the densities of other gases relative to the density of hydrogen. The hydrogen molecule is known to contain at least two atoms of hydrogen; and is not known to contain more than two atoms. The molecule of hydrogen therefore weighs two. The density of hydrogen is taken as one. The molecular weight of hydrogen being, thus, twice its density, it follows that the molecular weight of any gas is twice its density (compared with hydrogen).

So, in order to set the molecular weight of any body by the law of Avogadro we determine how many times heavier is any volume of the body, IN THE GASEOUS STATE, than the same volume of hydrogen, The density figure being determined it is multiplied by two; and the product is the molecular weight of the body (in its gaseous state).

This method for determining molecular weights is far simpler and much more direct than the chemical method; but it is only applicable to gases and to such liquids and solids as can be vaporized without decomposition.

The molecular weight of a body as set by purely chemical methods is always identical with the molecular weight determined by the application of Avogadro's law.

Examples.

Gas	Density (Hydrogen = 1)	Molecular Weight. Density \times 2	
Steam	9.	18.	
Hydrochloric Acid	18.25	36.5	
Ethane	15.	30.	
Ethyl Chloride	32.25	64.5	
&c.	&c.	&c.	

chemistry because they are the simplest of the compounds of carbon; and from two of them — methane, CH_4 ; and benzene, C_6H_6 — all of the other carbon compounds, may be considered as capable of being derived.

All of those carbon compounds that may be considered as capable of being derived from methane are called THE FATTY COMPOUNDS, or THE METHANE SERIES OF CARBON COMPOUNDS. The term fatty compounds merely refers to the fact that the natural fats belong to the series. Many bodies other than fats belong to the series. The nuclei of the molecules of the methane derivatives consist of OPEN CHAINS OF CARBON ATOMS.

All of those carbon compounds that may be considered as capable of being derived from benzene are called THE AROMATIC COMPOUNDS or THE BENZENE SERIES OF CARBON COMPOUNDS. The term AROMATIC COMPOUNDS refers to the fact that many of the benzene derivatives have an agreeable, spicy odor. The nuclei of the molecules of the benzene derivatives consist of CLOSED CHAINS OF CARBON ATOMS.

In the subjoined tables are given examples of hydrocarbons:

Fam- ily.	Name of Hydrocarbon.	Symbol	Boiling Point.	Sp. Grv.	Sat- uration.	Spe- cial Series	General Formulae.
	Methane	CH_4	-160°	gas			
F	Ethane	C_2H_6	$4@46 \text{ atm.}$	gas	Sat-	I.	$\text{C}_n\text{H}_{2n+2}$
A	Propane	C_3H_8	-17°	gas	ura-	M	
T	Butane	C_4H_{10}	1°	.60	ted	E.	
T	Pentane	C_5H_{12}	38°	.63		T	
Y	Hexane	C_6H_{14}	71°	.66	Mol-	H	
	Heptane	C_7H_{16}	99°	.70	ecu-	A	
C	Octane	C_8H_{18}	125°	.72	les.	N	
O	Nonane	C_9H_{20}	150°	.73		E	
M	Decane	$\text{C}_{10}\text{H}_{22}$	173°	.75			
P	Undecane	$\text{C}_{11}\text{H}_{24}$	195°	.77		S	
O	Dodecane	$\text{C}_{12}\text{H}_{26}$	214°	.77		E	
U	Tridecane	$\text{C}_{13}\text{H}_{28}$	234°	.78		R	
N	Eicosane	$\text{C}_{20}\text{H}_{42}$	205°	.78		I	
D	Pentatriacotane	$\text{C}_{35}\text{H}_{72}$	331°	.78		E	
S	&c.					S	
	Ethylene	C_2H_4	-105°	gas	Un-	II.	C_nH_{2n}
	Propylene	C_3H_6	Very low	gas	sat-	Et-	
	Butylene	C_4H_8	-5°	.63	ur-	yl-	
	Amylene	C_5H_{10}	30°	.67	ated.	ene	
	Melene	$\text{C}_{30}\text{H}_{60}$	375°	.89		Se-	
	&c.				Mol-	ries	

	ACETYLENE	C_2H_2	Very low	gas		III.	
	Allylene	C_3H_4	gas	gas	ecul-	ACT-	C_nH_{2n-2}
	Crotonylene	C_4H_6	18°	.65	es.	YLENE	
	Hexylene	C_6H_{10}	60°			SERIES	
	&c.						
ARO-	BENZENE	C_6H_6	81°	.89		IV.	
MATJO	TOLUENE	C_7H_8	110°	.89		BEN-	C_nH_{2n-6}
COM-	Xylene	C_8H_{10}	138°	.89		ZINE	
POU	Mesitylene	C_9H_{12}	165°	.87		SERIES	
NDS.	Cymene	$C_{10}H_{14}$	175°	.87			
	&c.						

S T R U C T U R A L F O R M U L A E .

The formulae assigned to the various hydrocarbons in the above table have been determined by the application of Avogadro's law; and by chemical reasonings such as have been outlined in the preceding pages. These formulae assign to the bodies their true molecular weights; and truly represent their elementary composition. Thus far the formulae are satisfactory. But when we consider the following points, it becomes easily manifest that our formulae are irrational — since they furnish no explanation for the observed facts:—

I. We have many examples of sets of hydrocarbons, the various members of each set having exactly the same molecular weights and elementary composition, yet showing more or less wide divergence in properties.

II. The various members of each series of hydrocarbons have certain chemical properties in common — which properties are not possessed by members of the other series.

For example:

We cannot add hydrogen or chlorine to any hydrocarbon belonging to the methane series. The members of the methane series of hydrocarbons are consequently spoken of as being SATURATED COMPOUNDS.

We can add TWO EQUIVALENTS of hydrogen to any member of the ethylene series of hydrocarbons. The members of this series are therefore UNSATURATED COMPOUNDS. Upon saturation with hydrogen, they become identical with members of the methane series.

We can add either TWO OR FOUR EQUIVALENTS of hydrogen to any member of the acetylene series of hydrocarbons — the members of this se—

ries being therefore unsaturated compounds. Upon adding two equivalents of hydrogen to a member of the acetylene series of hydrocarbons, we obtain a corresponding member of the ethylene series.

Upon the addition of four equivalents of hydrogen to a member of the acetylene series, we obtain a corresponding member of the methane series.

Some multiple of TWO EQUIVALENTS of hydrogen can be added to any one of the members of the benzene series of hydrocarbons — which are therefore unsaturated compounds. Upon adding two or more equivalents of hydrogen to a member of the benzene series, we do not obtain a member of any of the other series.

How are we to explain, and make readily apparent, the peculiarities of behavior we have just noted? This question we will now endeavor logically to answer. If the gross forms of matter be aggregations of molecules; and if these molecules be aggregations of atoms — it follows, unevitably, that the atoms in a molecule must be held together as a molecular unit by virtue of attractions between the atoms. It would most likely be of importance, therefore, for us to attempt to discover what atoms in a molecule thus mutually attract each other. We might, moreover, readily suspect that such knowledge, being gained, would furnish explanations for otherwise unexplained properties of the respective molecules.

But how are we to determine between what atoms are the attractive forces exerted? This knowledge is easy enough to obtain with reference to such molecules as contain only two atoms — for, of course, the attraction in such a molecule is between the two component atoms. When however, the molecule contains more than two atoms, the problem becomes a difficult one; and our desired knowledge is only obtained after a more or less complex system of reasoning.

We might, indeed, assume that every atom in a molecule is attracted by every other atom; and with varying quantities of attractive force, according to the respective spatial relations and natures of the atoms. It is quite probable that in a molecule each atom is attracted by all other atoms in the molecule — unless we conceive that certain molecules may be so large that particular pairs of atoms are separated by distances greater than that over which chemism can be operative. Nevertheless, the principal attractions in a molecule would undoubtedly be exerted between particular atoms only; and we are able to found a rational system of organic chemistry through correct deductions concerning the principal atomic attractions within the molecules of the various organic compounds.

Time and space will not permit an explanation of the reasons upon which are based all of the molecular STRUCTURES that will be stated in the following pages. The general method of reasoning will be outlined; and a few examples given.

Let us, then, start with the assumption that in a molecule the atomic attractions are not necessarily exerted equally between all of the atoms; but that the principal attractions may be exerted between certain atoms only. Begin by determining between what atoms the principal attractive forces are probably exerted in comparatively simple molecules.

Then build up, by SYNTHETIC processes, the more highly complex molecules from simpler molecules. Finally, draw the desired conclusions by rational analyses of the various syntheses.

The hydrogen molecule contains two atoms of hydrogen. We might express the molecule thus: $H - H$, the dash indicating the attractive force exerted between the two hydrogen atoms, holding them together as a molecular unit.

Such a formula for the hydrogen molecule might be called a STRUCTURAL FORMULA. Evidently, for what has been stated, this formula does not pretend to show the geometrical form of the molecule; but only that in the hydrogen molecule we have two hydrogen atoms held as a unit by virtue of their attractions for each other — which statement is, of course, a true one if the hydrogen molecule contains two atoms,

Each hydrogen atom might be written thus: $-H$, the dash representing its attractive force. Unless it be influenced by other forces than the chemical force, a hydrogen atom could not exist as an atom in the presence of another hydrogen atom. For the two attractive forces of the two hydrogen atoms would tend to neutralize or satisfy each other with the formation of a molecule of hydrogen. In other words, the condition $H - -H$ becomes at once the condition $H - H$.

The molecule of water contains two atoms of hydrogen and one atom of oxygen. We might represent the structure of the water molecule in any of the following ways:

I. $H - O - H$, or

II. $H - H - O$, or

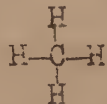
III. 

It will be evident that the first structure is the only probable one. For each hydrogen atom has the same attractive force; and in structure II we have represented the hydrogen atoms as being possessed of variable attractive forces. Structure III is discounted by our general knowledge of the compounds of hydrogen — this general knowledge pointing to the conclusion that an atom of hydrogen is never linked to more than one other atom of any kind. Therefore, while it cannot be denied that structures II and III might be possible, structure I is certainly highly probable. We will therefore write water $H - O - H$.

By so doing we have represented the oxygen atom as having just twice the attractive force; or, at least, the power of satisfying just twice the attractive force of one atom of hydrogen. The hydrogen atom

is therefore best written $=O$. The oxygen molecule contains two atoms of oxygen and would therefore be written $O=O$ basing our formula on the formula we have assigned to the molecule of hydrogen; and on the EQUIVALENCE of the hydrogen atom taken as unity.

The molecule of methane contains four atoms of hydrogen and one atom of carbon. For reasons quite analogous to those by which we fixed the structure of the water molecule, we should write the methane molecule

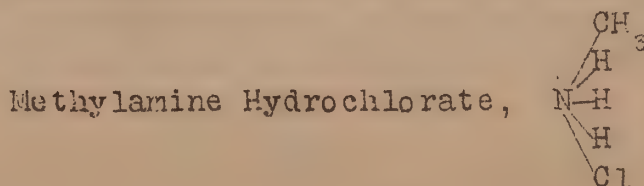
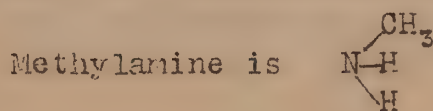
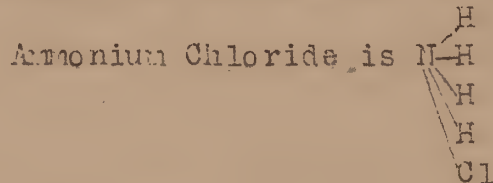
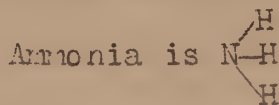


whereby we assign to the carbon atom the property of satisfying four atoms of hydrogen; and of being itself satisfied by them.

Since the affinity (or attractive force) of the oxygen atom is equivalent to that of two hydrogen atoms; and since the carbon atom is equivalent to four hydrogen atoms in this sense — it follows that one carbon atom should be FULLY satisfied by two oxygen atoms. That such is the fact is well illustrated by the compounds, carbon monoxide and carbon dioxide. For, while carbon monoxide may, indeed, exist alone, the compound readily combines with enough oxygen to form carbon dioxide. We cannot, however, more highly oxidize carbon dioxide. Carbon dioxide thus has the structure, $O=C=O$; which is in entire accordance with the structures $H-O-H$ and H

$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ The values 1, 2 and 4: represented by 1, 2 and 4 dashes, and expressing

the equivalence as above, of atoms of hydrogen, oxygen and carbon respectively, are called the VALENCIES of these atoms. All structural formulae for molecules are based upon our ideas as to the valencies of the constituent atoms. One atom that is very frequently met in the molecules of organic compounds shows a valency of three in some molecules; and a valency of five in others. It is the nitrogen atom. Nitrogen is an essential constituent of the organic bases, or alkalis. The free bases contain TRIVALENT NITROGEN; while their salts contain PENTAVALENT NITROGEN. The four examples that follow exhibit the type of molecules containing trivalent and pentavalent nitrogen.



In the subjoined table is given at a glance the valencies of all the atoms likely to be mentioned in the following pages.

TABLE OF VALENCIES.

ATOM	C	H	O	N	S	P	Cl	Br	I	Na	K	Ag	Ca	Mg	Zn.
USUAL VALENCE	4	1	2	3 and 5	2	3 and 5	1	1	1	1	1	1	2	2	2
IN MOLECULAR STRUCTURES.	$C \equiv H$	$H - O =$		$N \equiv$ $N \equiv$	$S =$	$P \equiv$ $P \equiv$	$Cl -$	$Br -$	$I -$	$Na -$	$K -$	$Ag -$	$Ca =$	$Mg =$	$Zn =$
RELATIVE IMPORTANCE.	The important elements.				Often Met						Occasional.				

Having decided that the structure of the methane molecule is $\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$ and having settled upon the valencies given for the various elements in the above table, we are ready for a study of those synthetic methods from which we may deduce the structures of the molecules of other organic compounds. (The student must not fail to remember that the structural formulae about to be given express nothing whatever concerning the SPATIAL relations between the atoms in a molecule — and, it may be remarked in passing, that upon the subject of the spatial relations of atoms we have only meagre and dubious knowledge).

If the structure of the methane molecule be examined, its perfect structural symmetry will be at once apparent — each hydrogen atom being united to a $-CH_3$ group of atoms.

It is possible to replace one of the hydrogen atoms in the methane molecule by an atom of chlorine giving the compound CH_3Cl . This compound is obtained by exposing a mixture of equal volumes of chlorine and methane to the action of sunlight.



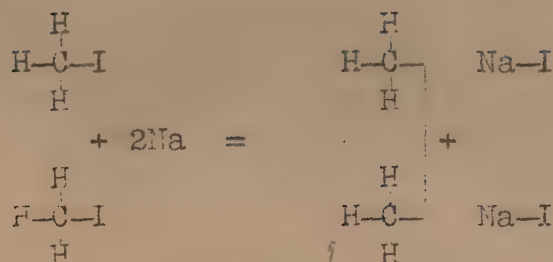
From the perfect structural symmetry of CH_4 , it would be expected that the same compound would result, no matter which of the four hydrogen atoms be replaced by an atom of chlorine. Now, as a matter of fact, only ONE monochlor-methane is known. This fact, then, strengthens our ideas as to the structure of the methane molecule.

From methane we can prepare a monoiodomethane, CH_3I . Now we have found that when sodium acts upon monoiodomethane, sodium iodide

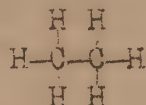
and ethane are formed — the reaction being $2CH_3I + 2Na = C_2H_6 + 2NaI$.

If instead of stating the reaction as above, we will write the structural formulae for the molecules concerned, the reaction would

appear thus:



Ethane has thus been proven to have the molecular structure

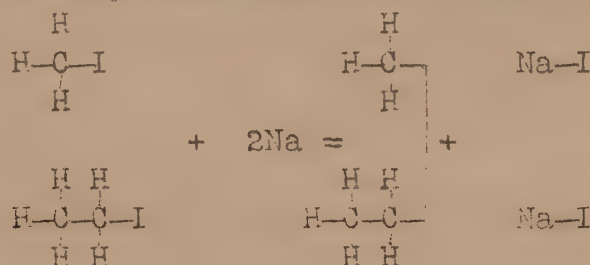


Upon examining the structure of the ethane molecule, it is seen to exhibit a perfect structural symmetry — as follows:

- Structural symmetry of the ethane molecule.
- I. Each hydrogen atom is combined with a $-\text{CH}_2-$ group, which group is in turn combined with a $-\text{CH}_3$ group. All of the hydrogen atoms are therefore structurally symmetrical.
 - II. Each carbon atom is combined with two hydrogen atoms with a $-\text{CH}_3$ group. The carbon atoms are therefore structurally symmetrical.

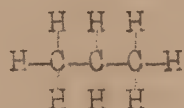
From the symmetry of the ethane molecule it would be expected that more than one monoiodoethane could not be obtained. As a matter of fact only one $\text{C}_2\text{H}_5\text{I}$ is known. Here again, our ideas as to the correctness of our structural formulae are strengthened.

Sodium acting upon a mixture of equivalent quantities of CH_3I and $\text{C}_2\text{H}_5\text{I}$ gives us propane and sodium iodide. Expressing the reaction by the use of our already determined structural formulae we would have



Propane

has thus been proven to have the structure —



An examination of the structure of the propane molecule shows that the perfect structural symmetry observed in methane and ethane, has disappeared in propane,

Lack of symmetry in the propane

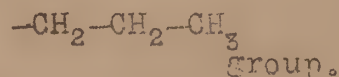
- I. The six hydrogen atoms that are attached to the two terminal carbon atoms are symmetrical with respect to each other; but are unsymmetrical with the two hydrogen atoms that are attached to the

intermediate carbon atom.

- II. The two hydrogen atoms that are attached to the intermediate carbon atom are symmetrical with respect to each other; but are unsymmetrical with respect to the six hydrogen atoms that are attached to the two terminal carbon atoms.
- III. The two terminal carbon atoms are symmetrical with respect to each other; but are unsymmetrical with respect to the intermediate carbon atom.

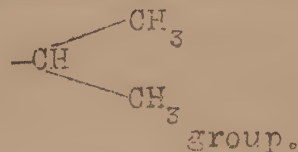
Symmetrical relations of the six hydrogen atoms that are attached to the two terminal carbon atoms.

Each hydrogen atom is attached to a



Symmetrical relations of the two hydrogen atoms that are attached to the intermediate carbon atom.

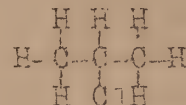
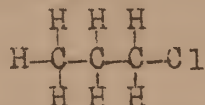
Each hydrogen atom is attached to a



Symmetrical relations of the two terminal carbon atoms.

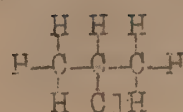
Each carbon atom is separately attached to three hydrogen atoms and to a $\text{---CH}_2\text{---CH}_3$ group.

From the lack of symmetry of the propane molecule we should expect that the two mono-chloropropanes,



would be bodies having different properties. That such is the fact experiment has clearly enough shown. Thus, for example:—

Body	Name	Specific Gravity.	Boiling Point.	Action of moist silver oxide and oxidation of the resulting compound.
$\begin{array}{c} \text{H} \text{ H} \text{ H} \\ \quad \quad \\ \text{H---C---C---C---Cl} \\ \quad \quad \\ \text{H} \text{ H} \text{ H} \end{array}$	Normal propyl chloride.	.91	46°	Becomes an alcohol which upon oxidation becomes an aldehyde, which by oxidation becomes an acid. &c.

Isopropyl
chloride.

.88

38°

Becomes an alcohol
which upon oxida-
tion becomes a ke-
tone, which cannot,
by further oxida-
tion become the
above acid.&c.

We should think further, that more than two monochloropropanes could not be obtained. Such is the fact, It will, therefore, be seen that our structural formulae for propane and its derivatives, have not only led us to expect established facts; but have also furnished us with explanations for observed differences in two bodies that have the same composition and the same molecular weights.

I S O M E R I S M .

Chemical studies of matter furnish us, commonly, with examples of series of two or more bodies that have the same elementary composition but nevertheless show divergence in their properties. Such bodies are said to be ISOMERIC with regard to each other.

I. Certain elements habitually exhibit themselves in more than one form — such as carbon in charcoal, graphite and diamond. This species of isomerism is due to differences in the molecular weights of the various bodies. Isomerism of an element is termed ALLOTROPY.

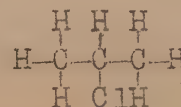
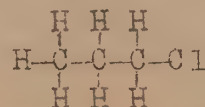
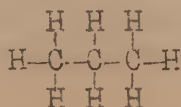
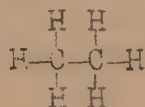
II. Certain compounds that exhibit isomerism are readily shown to have different molecular weights; and the observed isomerism is thus explained. Thus, formaldehyde and lactic acid have the same percentage composition; but the molecule of lactic acid is three times as heavy as the molecule of formaldehyde.

Formaldehyde, CH_2O Lactic Acid, $\text{C}_3\text{H}_6\text{O}_3$

III. We have many examples of sets of bodies that have not only the same composition; but have also the same molecular weights. Thus, we have two lactic acids — each having the formula $\text{C}_3\text{H}_6\text{O}_3$. Such bodies are said to be TRUE isomeric bodies. As has been seen in the preceding pages, the observed differences in properties of certain of the true isomeric bodies are most probably due to; and are certainly readily and rationally explained by structural differences in the respective molecules.

SIMPLEST METHOD FOR WRITING STRUCTURAL FORMULAE.

The formulae we have just established: to wit,



are very cumbrous; and a shorter form of expression becomes desirable. Such shortened formulae are found in the expressions



Page 18.

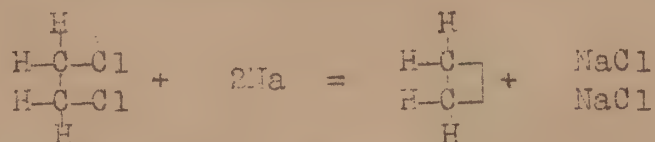
In these formulae it is only necessary to remember that each hydrogen atom is separately connected with the adjacent carbon atom on the same side of the period; and that the periods signify the bonds between the carbon atoms.

ALL HYDROCARBONS BELONGING TO THE METHANE, ETHYLENE AND ACETYLENE SERIES, CONSIDERED AS DERIVATIVES OF THE SINGLE HYDROCARBON METHANE.

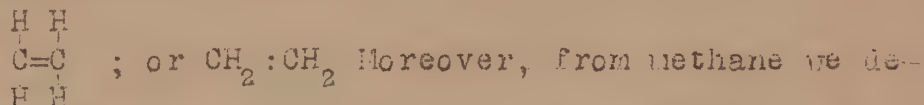
It has been seen in the foregoing pages that ethane and propane may be derived from methane. By similar processes we can derive other members of the methane series from methane.

The bodies $\text{CH}_3.\text{CHCl}_2$ and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$, which can be obtained from ethane are not symmetrical. We should therefore expect them to exhibit differences in their properties. Experiment shows such to be the fact. Again our structures predict and explain the facts.

$\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ being acted upon by sodium gives us ethylene and sodium chloride. Thus:

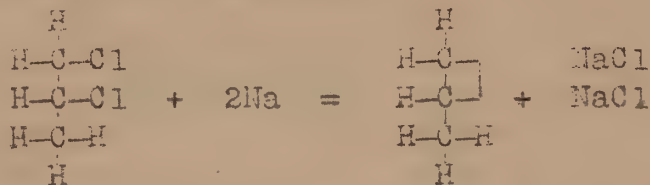


Ethylene has consequently the formula



derived ethane; from ethane we derived $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$; and from $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ we derived ethylene. Ethylene is therefore conveniently considered as a derivative of methane.

From propane we have $\text{CH}_2\text{Cl}.\text{CHCl}.\text{CH}_3$. This body acted upon by sodium could give the following reaction:

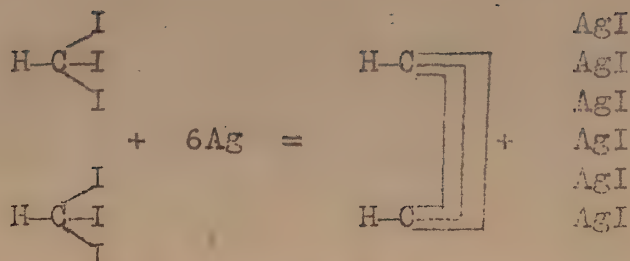


But the body C_3H_6 is propylene. Propylene is therefore a methane derivative; and its molecule has the structure $\text{CH}_2:\text{CH}.\text{CH}_3$.

In a similar manner the formula of butylene could be shown to be $\text{CH}_2:\text{CH}.\text{CH}_2.\text{CH}_3$ —and so on through various members of the ethylene series.

From methane we may prepare CHI_3 . This body acted upon by silver furnishes acetylene and silver iodide.

Thus:



Acetylene has therefore the formula $\text{H}-\text{C}\equiv\text{C}-\text{H}$; or $\text{CH}:\text{CH}$; and is a derivative of methane.

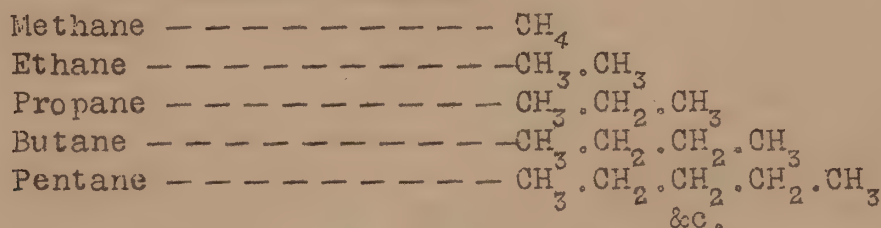
Allylene may be prepared by the action of sodium on the propane derivative $\text{CHCl}_2.\text{CCl}_2.\text{CH}_3$. Its formula is thus shown to be $\text{CH}:\text{C}.\text{CH}_3$; and it is a derivative of methane. We might make other syntheses of hydrocarbons belonging to the acetylene series with analogous results.

STRUCTURAL CHARACTERISTICS OF THE METHANE, ETHYLENE AND ACETYLENE

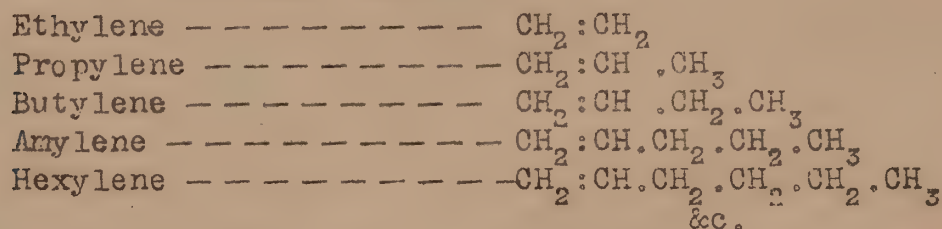
SERIES OF COMPOUNDS.

In the light of the knowledge we have thus far gained in our studies of the structures of the hydrocarbon molecules we are enabled to write the following formulae:

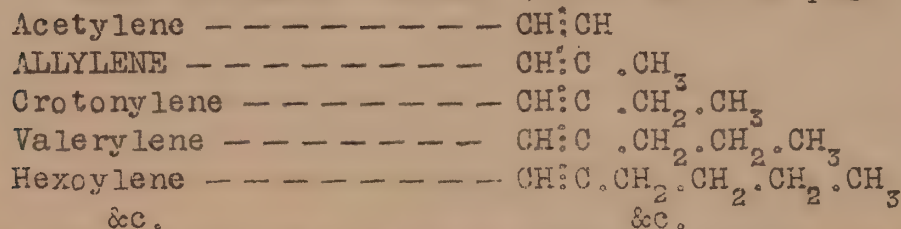
I. METHANE SERIES. --



II. ETHYLENE SERIES. --



III. ACETYLENE SERIES (refer also to page 22.)



We observe that in all of the above series of molecules the nuclei are OPEN CHAINS OF CARBON ATOMS.

In the methane series ALL of the linkages between the carbon atoms are by SINGLE BONDS. Such a carbon nucleus is the distinctive

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structural characteristic of all carbon compounds DIRECTLY related to the methane series of hydrocarbons.

In every molecule of the Ethylene series of hydrocarbons it will be observed that there are TWO carbon atoms that are linked together by a DOUBLE BOND. Such a carbon nucleus is the distinctive structural characteristic of all organic compounds that are DIRECTLY related to the ethylene series of hydrocarbons.

In every molecule of the Acetylene series of hydrocarbons, it will be observed that there are TWO carbon atoms that are linked together by a TRIPLE BOND. Such a carbon nucleus is the distinctive structural characteristic of all organic compounds that are DIRECTLY related to the acetylene series of hydrocarbons. (With regard to the acetylene series refer also to page 22.)

A MULTITUDE OF FACTS IN THE CHEMISTRY OF THE CARBON COMPOUNDS FIND RATIONAL EXPLANATION IN THE STRUCTURAL RELATION JUST DISCUSSED.

ISOMERISM AMONG THE HYDROCARBONS.

The term isomerism has already been defined; and we have observed several examples and the explanations therefore in such bodies as normal propyl chloride and isopropyl chloride. Among the various members of the hydrocarbons we find exceedingly numerous examples of true isomeric bodies. The few examples of possible structures of hydrocarbon molecules, that are given below will be understood if the preceding pages have been carefully studied. It is only necessary to remember that the isomerism among the various bodies are the results of structural differences in the respective molecules.

EXAMPLES OF ISOMERISM.

M E T H A N E S E R I E S	GENERAL NAME.	GENERAL FORMULA	STRUCTURES AND SPECIAL NAMES.
	Methane	CH_4	Only one possible.
	ETHANE	C_2H_6	$\text{CH}_3.\text{CH}_3$ Only one possible.
	Propane	C_3H_8	$\text{CH}_3.\text{CH}_2.\text{CH}_3$ Only one possible.
	Butane	C_4H_{10}	Two are possible.
			Normal Butane $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_3$
			Isobutane $\text{CH}_3.\text{CH} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$

E T H S Y E L R E I W E S	Pentane	C_5H_{12}	Three are possible; Normal Pentane $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ Isopentane $CH_3 \cdot CH_2 \cdot CH \begin{array}{l} \nearrow CH_3 \\ \searrow CH_3 \end{array}$ Tetramethyl Methane $\begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ CH_3 \quad CH_3 \end{array}$
	Hexane	C_6H_{14}	Five are possible: Normal Hexane $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ Propyl Dimethyl Methane $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH \begin{array}{l} \nearrow CH_3 \\ \searrow CH_3 \end{array}$ Di-isopropyl $\begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \cdot CH \\ \diagup \quad \diagdown \\ CH_3 \quad CH_3 \end{array}$ Diethyl Methyl Methane $CH_3 \cdot CH \begin{array}{l} \nearrow CH_2 \cdot CH_3 \\ \searrow CH_2 \cdot CH_3 \end{array}$ Trimethyl Ethyl Methane $\begin{array}{c} CH_3 \quad CH_2 \cdot CH_3 \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ CH_3 \quad CH_3 \end{array}$
	&c.	&c.	&c.
	Ethylene	C_2H_4	$CH_2:CH_2$ Only one possible.
	Propylene	C_3H_6	$CH_2:CH \cdot CH_3$ Only one possible.
	Butylene	C_4H_8	Three are possible: Normal Butylene, $CH_2:CH \cdot CH_2 \cdot CH_3$ Isobutylene, $CH_3 \cdot CH:CH \cdot CH_3$ Pseudobutylene $CH_2:C \begin{array}{l} \nearrow CH_3 \\ \searrow CH_3 \end{array}$
	&c.	&c.	&c.
	&c.	&c.	&c.
	&c.	&c.	&c.
	&c.	&c.	&c.
	&c.	&c.	&c.

A	True	Acetylene	C_2H_2	$CH:CH$ Only one possible.
C	Acet-			
E	yl-	Allylene	C_3H_4	$CH:C.CH_3$ Only one possible.
T	enes.			
Y		Crotonylene	C_4H_6	Two are possible:
L				Normal Crotonylene $CH:C.CH_2.CH_3$
E				
N				Dimethyl Acetylene $CH_3.C:C.CH_3$
E				
S	Isomer-	Certain of the hydrocarbons have carbon nuclei contain-		
E	ic	ing two sets of two carbon atoms united by double linkages.		
R		These hydrocarbons have therefore the general formula C_nH_{2n-2}		
I	Acet-	See below.		
E	yl-	Isomeric		
S	enes.	Allylene	C_3H_4	$CH_2:C:CH_2$
		Isomeric	C_4H_6	Two are possible:
		Crotonylene		Diethylene $CH_2=CH-CH=CH_2$
				Methylene Propylene $CH_2=C=CH.CH_3$

REMARKS UPON THE DERIVATIVES OF THE HYDROCARBONS.

The members of the methane series of hydrocarbons, being saturated compounds, can form derivatives only by REPLACEMENT of hydrogen atoms by other atoms or groups of atoms.

The members of the ethylene series of hydrocarbons, being unsaturated compounds, can form derivatives both by the replacement of hydrogen atoms by other atoms or groups of atoms; and by the ADDI-

TION of atoms or groups of atoms to the respective molecules. When addition occurs, the double linkages disappear, and the resulting compounds belong to the methane series of compounds. Thus, taking ethylene as an example:

By replacement $CHCl:CH_2$
 By addition $CH_2Cl.CH_2Cl$

The remarks above concerning the ethylene series, hold true for the acetylene series, excepting as follows:—While we can add only TWO affinities to molecules of the ethylenes, we can add either TWO or FOUR affinities to molecules of the acetylenes. Thus, taking acetylene for an example:

By replacement $CH:CBr$
 By addition of two affinities $CHBr:CHBr$
 By addition of four affinities $CHBr_2.CHBr_2$

WELL KNOWN HYDROCARBONS.

The best known and most widely used hydrocarbons are those that occur in petroleum. Closely allied to petroleum are natural gas and ozokerite (mineral wax). These bodies consist of mixtures of hydrocarbons of varying boiling points — belonging for the most part to the methane series. Petroleum or [“]rock oil[”] is seldom used in the exact condition that it occurs in nature. The crude material is usually subjected to a process of FRACTIONAL DISTILLATION, by which means the portions having different boiling points are more or less completely separated from each other. In addition to the fractional distillation, the fractions are deodorized and decolorized by successive treatments with sulphuric acid, caustic soda and water and filtration through animal charcoal. The principal products are called, commercially:

CYMOGENE — Gaseous at ordinary temperatures. Boiling point 0° . Used in ice machines.

RHIGOLENE — Boils at 18° ; and has been used as an anaesthetic.

PETROLEUM ETHER — Boiling point from 70° to 80° . Used as a solvent for gums and fats.

GASOLINE — Nearly same as petroleum ether. Used in [“]gas machines[”]

NAPHTHA — Boiling point from 80° to 110° . Used for burning in vapor stoves and street lamps, and as a solvent in making varnishes &c.

LIGROINE — B.P. 80° to 120° . Solvent for pharmaceutical purposes.

BENZINE (not Benzene) — B.P. 120° to 150° . Substitute for turpentine and for cleaning materials from grease.

KEROSINE — Graded mainly by the temperature at which it ignites. Good kerosene has a fire test of not less than 150° F.

LUBRICATING OIL — The more viscous portions of petroleum are used for lubricating purposes.

VASELINE, PETROLATUM — A special hydrocarbon mixture melting at 40° to 50° and obtained by distillation in vacuum apparatus.

PARAFFINE WAXES — Petroleum hydrocarbons that are solids at ordinary temperatures.

The hydrocarbons belonging to the methane series enter into chemical reactions with reluctance — hence their name, PARAFFINS (from parum — affinis). Petroleum consists mainly of paraffins; and among the best known of the paraffins are the gases methane, or marsh gas (CH_4); and ethane, or olefiant gas (C_2H_6).

The gas acetylene (C_2H_2) has lately become a very well known hydrocarbon. The flame of burning acetylene is the most brilliant of all simple gas flames. Acetylene is now produced on a large scale by the action of water on calcium carbide.



Calcium carbide is produced in the electric furnace from mixtures of limestone with coal.

HALOGEN DERIVATIVES OF THE HYDROCARBONS.

These are among the simplest of the derivatives of the hydrocarbons. They result by the direct action of the halogens upon the hydrocarbons; or by the action of the halogen hydrides (HCl, HBr, HI) upon the alcohols.

Examples

of

formation

of

halogen

derivatives.



Prominent among the halogen derivatives of the hydrocarbons are the following:

Methyl Chloride,	CH_3Cl ;	Ethylene Chloride,	$\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$;
Ethyl Chloride,	$\text{C}_2\text{H}_5\text{Cl}$;	Ethylidene Chloride,	$\text{CH}_3.\text{CHCl}_2$;
Methyl Bromide,	CH_3Br ;	Chloroform,	— — — — CHCl_3 ;
Ethyl Bromide,	$\text{C}_2\text{H}_5\text{Br}$;	Iodoform,	— — — — CHI_3 ; (yellow
Methyl Iodide,	CH_3I ;	crystalline solid with peculiar odor)	
Ethyl Iodide,	$\text{C}_2\text{H}_5\text{I}$;	Bromoform,	CHBr_3 .

The above compounds are, for the most part, agreeable ethereal liquids, having anaesthetic and antiseptic properties.

A L C O H O L S .

It has been seen that the halogen derivatives of the hydrocarbons may be considered as derived from the hydrocarbons themselves by the replacement of one or more of the hydrogen atoms in hydrocarbon molecules by one or more halogen atoms.

Thus From Methane, CH_4 , we obtain Methyl Chloride CH_3Cl .

From Ethane, C_2H_6 , we obtain Ethyl Chloride $\text{C}_2\text{H}_5\text{Cl}$.

From Propane, C_3H_8 we obtain Propyl Chloride $\text{C}_3\text{H}_7\text{Cl}$

&c.

&c.

Now it is possible to replace indirectly one or more of the hydrogen atoms of hydrocarbons by one or more -O-H groups. The resultant compounds are called ALCOHOLS. Presuming all the necessary steps to be known we could obtain as follows:

Thus (Examples of alcohols)	From Methane, CH_4 , we obtain Methyl Alcohol, CH_3OH
	From Ethane, C_2H_6 , we obtain Ethyl Alcohol, $\text{C}_2\text{H}_5\text{OH}$
	From Propane, C_3H_8 , we obtain Propyl Alcohol, $\text{C}_3\text{H}_7\text{OH}$
	From Ethane, C_2H_6 , we obtain Ethylene Glycol, $\text{C}_2\text{H}_4(\text{OH})_2$
	From Propane, C_3H_8 , we obtain Glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$
	From Butane, C_4H_{10} , we obtain Erythrite, $\text{C}_4\text{H}_6(\text{OH})_4$
	From Pentane, C_5H_{12} , we obtain Arabite, $\text{C}_5\text{H}_7(\text{OH})_5$
	From Hexane, C_6H_{14} , we obtain Mannite, $\text{C}_6\text{H}_8(\text{OH})_6$

In order to bring about the replacement of -OH groups for H atoms in hydrocarbons we must, as intimated above, resort to intermediate steps. For instance: From methane we can prepare methyl chloride, CH_3Cl

by the direct action of chlorine upon methane. We may then act upon methyl chloride with moist silver oxide (which is equivalent to silver hydroxide, AgOH) — thereby obtaining methyl alcohol.

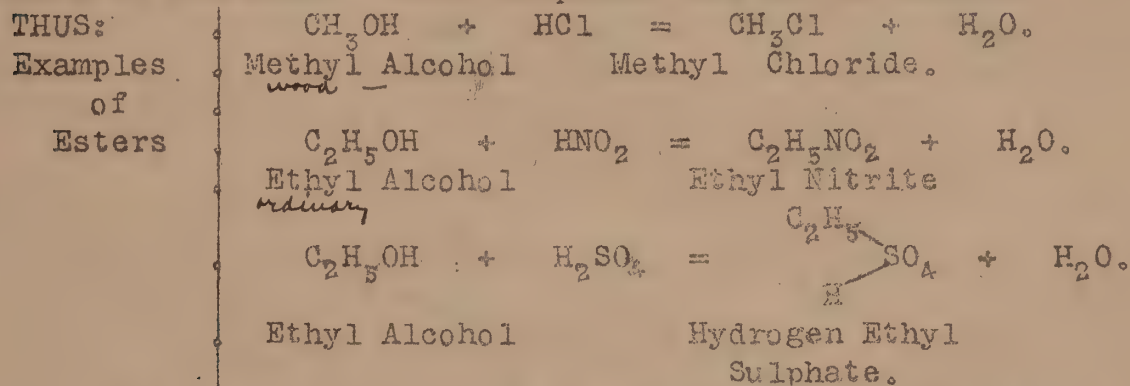


Again, from ethyl iodide and silver hydroxide we can obtain ethyl alcohol.

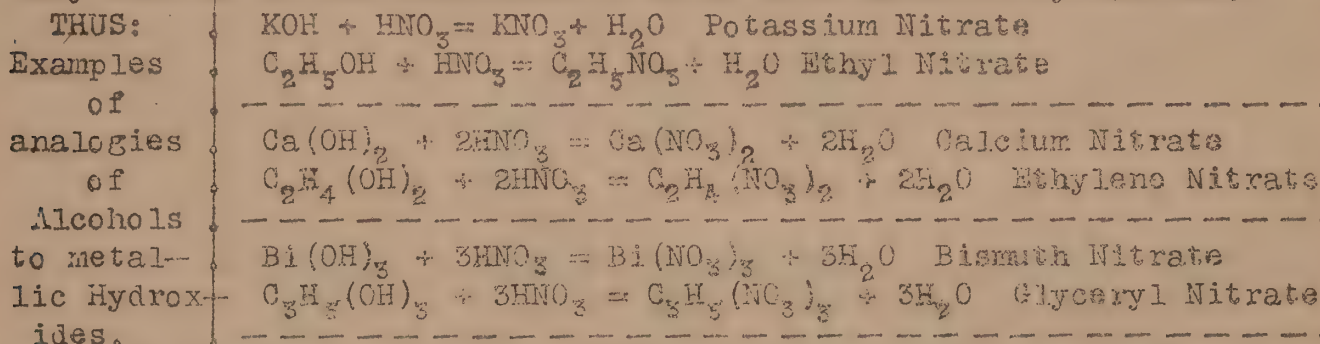


Further, by more or less complex processes, we may derive various other alcohols from their corresponding hydrocarbons; or show such relations.

Those alcohols that have comparatively low molecular weights are liquids which mix readily with water. As the molecular weights increase, we pass through oily liquids; and, finally, to fat like solids without odor or taste. THE MOST MARKED COMMON CHEMICAL CHARACTERISTIC OF THE ALCOHOLS IS THAT THEY REACT WITH ACIDS TO FORM COMPOUNDS ANALOGOUS TO THE SALTS. Such compounds are called ESTERS.



It will be observed that the reactions of acids with alcohols are very similar to the reactions of acids with metallic hydroxides.



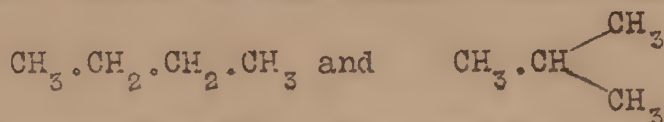
The alcohols that have been derived from the methane series of hydrocarbons by the replacement of one hydrogen atom by an $-\text{OH}$ group, are analogous to the alkaline hydroxides in their reactions with acids consequently the groups $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ &c., have been called ALKYL groups. The student must not, however, make the mistake of thinking that the esters are true salts; or that the alkyls are powerfully basic like the alkaline metals and ammonium. The alkyls are but feebly basic — resembling, in this respect, aluminum. The esters are more or less readily or completely decomposed by water, steam or caustic alkalis—any such decomposition being termed a SAPONIFICATION. Let it

be remembered also that the term ether is very often used (especially by pharmacists) as synonymous with the term ester. We reserve, in a systematic organic chemistry, the term ether as applicable ONLY to a group of organic compounds analogous in structure to the metallic oxides. Saponification and ethers will be discussed more fully in another place.

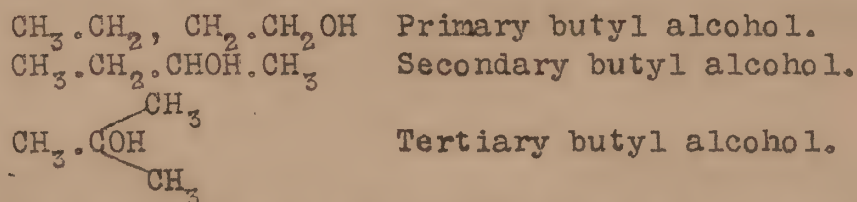
CLASSIFICATION OF ALCOHOLS.

Alcohols are classified, according to the number of $-OH$ groups in their molecules, into monohydric, dihydric, trihydric, tetrahydric, pentahydric, hexahydric alcohols, &c.

Like other derivatives of the hydrocarbons the alcohols exhibit among their number numerous sets of isomers — the isomerism depending, as in our previous studies, on differences in structure of the individual alcohols. In order to understand how isomerism may occur among the alcohols, let us examine butane, C_4H_{10} ; and butyl alcohol, C_4H_9OH . Butane itself exists in two isomeric modifications.



Butane has, therefore three distinct kinds of hydrocarbon groups: viz. $-CH_3$, $=CH_2$ and $\equiv CH$ groups. If an H of a $-CH_3$ group be replaced by $-OH$ we have one of the isomeric butyl alcohols. If an H of a $=CH_2$ group be replaced by $-OH$, we have another of the isomeric butyl alcohols. If an H of a $\equiv CH$ group be replaced by an $-OH$ group, we have the third of the isomeric butyl alcohols. The three isomeric butyl alcohols are, therefore:



From the foregoing remarks upon the butyl alcohols, as examples, it will be seen that we may have THREE CLASSES OF — ALCOHOL GROUPS: viz, $-CH_2OH$, $=CHOH$ and $\equiv COH$ groups. The group $-CH_2OH$ is called the primary alcohol group; and all monohydric alcohols that contain a $-CH_2OH$ group are called PRIMARY ALCOHOLS. The group $=CHOH$ is called the secondary alcohol group; and all monohydric alcohols that contain a $=CHOH$ group are called SECONDARY ALCOHOLS. The group $\equiv COH$ is called the tertiary alcohol group; and all monohydric alcohols that contain a $\equiv COH$ group are called TERTIARY ALCOHOLS.

The primary, secondary and tertiary alcohols exhibit remarkable differences in the products obtainable from them by processes of oxidation. Upon oxidation, the primary alcohols first become neutral bodies called ALDEHYDES. Oxidation of the aldehydes gives us the ORGANIC

ACIDS, which cannot be oxidized further without the splitting up of the respective carbon nuclei. Upon oxidation, the secondary alcohols first furnish neutral bodies termed KETONES; and further oxidation breaks up the carbon nuclei. The tertiary alcohols yield no characteristic oxidation products,

Illustrating
the oxidations
of alcohols.

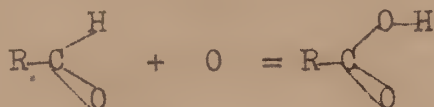
PRIMARY.



Alcohol

Aldehyde

R— means any
monovalent
group.

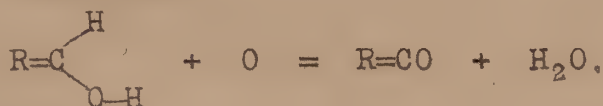


Aldehyde

Acid.

R= means any
divalent
group.

SECONDARY.



Alcohol

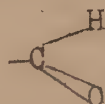
Ketone

R≡ means any
trivalent
group.

TERTIARY

$\text{R}\equiv\text{C}-\text{OH}$ Gives no characteristic oxidation
Alcohol product.

The aldehyde group is therefore



More commonly written

simply $-\text{CHO}$

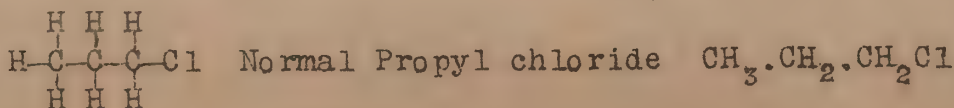
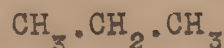
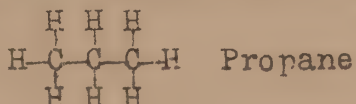
The organic acid group is therefore
written $-\text{COOH}$; or $-\text{CO}_2\text{H}$; and called
CARBOXYL.

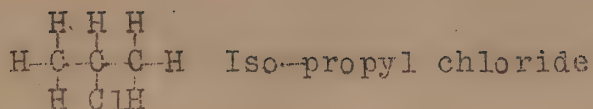


More commonly

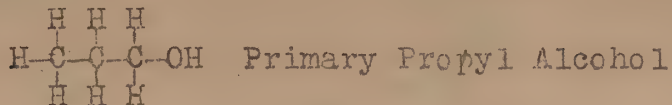
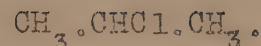
The ketone group is therefore $=\text{C}=\text{O}$. More commonly written $=\text{CO}$.

The student may be aided in understanding much that has been said in the preceding pages if he will examine the following evolution of certain derivatives of propane:

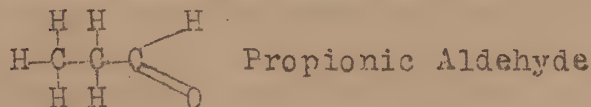
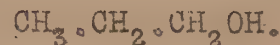




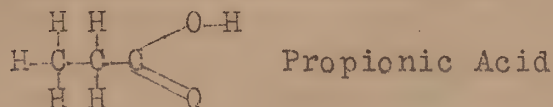
Iso-propyl chloride



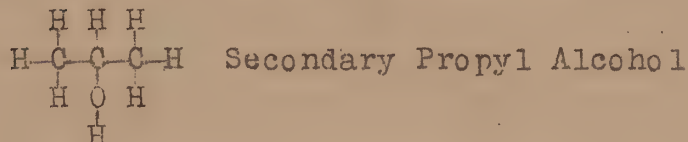
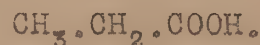
Primary Propyl Alcohol



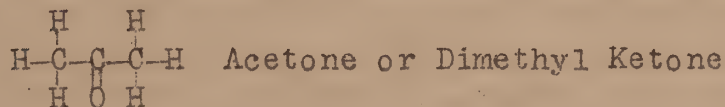
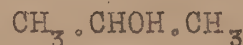
Propionic Aldehyde



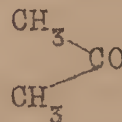
Propionic Acid



Secondary Propyl Alcohol



Acetone or Dimethyl Ketone



P R O M I N E N T A L C O H O L S .

METHYL ALCOHOL, or WOOD SPIRIT, CH_3OH is obtained on a large scale by the destructive distillation of wood during the process of making retort charcoal. The valuable products of this distillation are mainly methyl alcohol, acetic acid, acetone, creasote and wood tar. The methyl alcohol is obtained from this mixture by distillation of the fractions of medium volatility over lime.

Methyl alcohol, when casually examined, resembles ordinary alcohol in a general way; but may be easily distinguished by its peculiar odor.

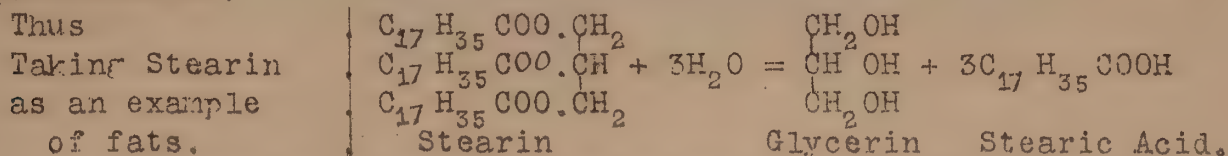
ETHYL ALCOHOL, $\text{CH}_3.\text{CH}_2\text{OH}$, is common alcohol. It is obtained by the spirituous fermentation of saccharine liquids. The fermented liquids are distilled -- ethyl alcohol appearing as a distillate.

THE FUSEL OILS so called are always produced during ordinary alcoholic fermentations. These oils are principally mixtures of butyl, amyl and propyl alcohols. They are much more poisonous than ethyl alcohol.

ETHYLENE GLYCOL, $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$, is the most prominent of the dihydric alcohols. It is a colorless, thick liquid soluble in water.

GLYCERINE, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$, is the leading example of the trihydric alcohols.

Glycerine is prepared from fats and oils, which are esters of Glycerine, by distillation of the fats with superheated steam (a saponification).



Pure glycerine is a thick, colorless, sweet liquid that absorbs water energetically and easily dissolves in water.

ERYTHROL, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$, the type of tetrahydric alcohols occurs in combination in many lichens, from which it may be prepared. Erythrol is a crystalline, sweet, solid, soluble in water.

ARABITE, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$ Gum Arabic contains an aldehyde of arabite, called ARABINOSE. Arabite is interesting as being the leading pentahydric alcohol. It is a sweet crystalline solid.

MANNITOL, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$, from manna, serves to illustrate the hexahydric alcohols. It is produced during the mucous fermentation of sugars; and is a very sweet, soluble, crystalline solid.

PROMINENT ALDEHYDES AND KETONES.

FORMALDEHYDE, $\text{H}.\text{CHO}$, is so named because on oxidation it becomes formic acid. Formaldehyde is the simplest of the aldehydes. It has lately become of the greatest interest to the medical profession because of its being the most convenient gaseous germicidal agent known. It is prepared by burning methyl alcohol with a regulated quantity of air.



The gaseous formaldehyde thus formed is dissolved in water for convenient use; or else converted into PARA-FORMALDEHYDE, $(\text{CH}_2\text{O})_3$. Paraformaldehyde is a white solid, valuable mainly because upon being heated with water to 130° , it furnishes formaldehyde gas.

ACETALDEHYDE, CH_3CHO , is the body commonly called simple, "aldehyde". Acetaldehyde is a volatile liquid that occurs in the first "runnings" of the stills during the manufacture of ethyl alcohol.

CHLORAL, CCl_3CHO ; and CHLORAL HYDRATE, $\text{CCl}_3.\text{CHO} + \text{H}_2\text{O}$ are important derivatives of acetaldehyde. Chloral is an oily, pungent smelling liquid that combines with water to form solid, crystalline chloral hydrate.

ACETONE, or DIMETHYL KETONE, $\text{CH}_3.\text{CO}.\text{CH}_3$, is the simplest of the ketones and a prominent member of the family. Its occurrence with wood spirit has already been noted. Acetone is a mobile, volatile liquid of peculiar odor; and is an occasional constituent of pathological urines

THE CARBOHYDRATES.

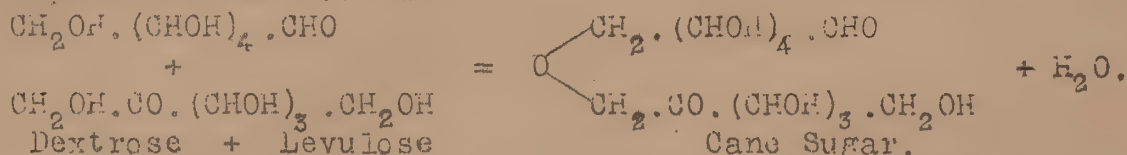
The carbohydrates are a most important and widely distributed class of compounds. Molecules of carbohydrates contain six or a multiple of six carbon atoms and hydrogen and oxygen atoms — the hydrogen

atoms being twice as numerous as the oxygen atoms. The carbohydrates are divided naturally into three groups, which groups have been called the monosaccharides, the disaccharides, and the polysaccharides. Of these carbohydrate groups, the monosaccharides are the parent bodies. They have the general formula, $C_6H_{12}O_6$ and are either aldehydes or ketones of the hexahydric alcohols (like mannite).

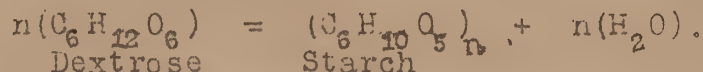
Thus: $CH_2OH.(CHOH)_4.CHO$ Dextrose
 $CH_2OH.CO.(CHOH)_3.CH_2OH$ Levulose. } Two important Monosaccharides.

The disaccharides are ethereal anhydrides of the monosaccharides.

The formation of cane sugar (the most important disaccharide) may likely be represented as follows:



The polysaccharides are anhydrides of the monosaccharides. The formation of starch (the most important polysaccharide) may be represented as follows:



(For further information concerning the carbohydrates consult Halliburton.)

PROMINENT ACIDS BELONGING TO THE METHANE DERIVATIVES.

FORMIC ACID, $H.COOH$, begins the list. It corresponds to methyl alcohol and formaldehyde. Was so named because it was first obtained by distilling ants. Formic acid is found free in many insects. It is a rather heavy liquid (sp. gr. 1.25) with pungent odor; and blisters the skin.

ACETIC ACID, CH_3COOH , is the essential acid in vinegar. Acetic acid is produced on a large scale by the fermentation of many organic substances, particularly of ethyl alcohol, in the presence of air. Acetic acid occurs among the products obtained during the destructive distillation of wood - this process being the principal source of supply of this important acid.

Absolutely pure acetic acid is a crystalline white solid at temperatures lower than 17° ; and because of this fact is called "Glacial" acetic acid.

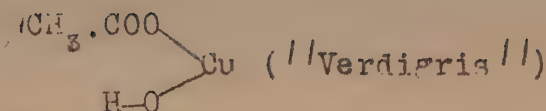
Some industrially well known metallic acetates are:

Sodium Acetate, $CH_3.COONa$

Ferrous Acetate $\begin{array}{c} CH_3.COO \\ \diagup \quad \diagdown \\ Fe \end{array}$

Lead Acetate, $\begin{array}{c} CH_3.COO \\ \diagup \quad \diagdown \\ Pb \end{array}$ ("Sugar of lead").

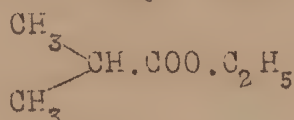
Basic Cupric Acetate



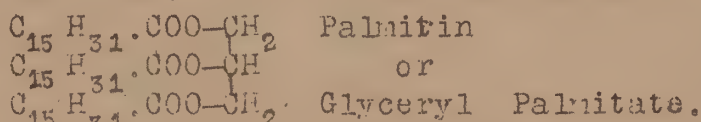
Normal Butyric Acid, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, is produced by the //butyric// fermentation of sugar or starches — such fermentation being brought about through the activity of the butyl bacillus and bacillus subtilis. Butter fat contains the butyl ester of glycerine.

Butyric acid is a thick, rancid smelling liquid.

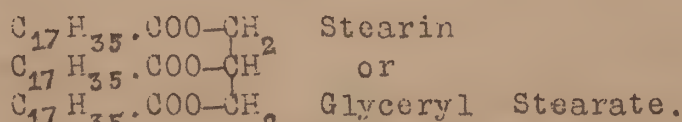
CROTON OIL contains the ethyl ester of iso-butyric acid,



PALMITIC ACID, $\text{C}_{15}\text{H}_{31}\text{COOH}$, occurs as the glycerol ester called PALMITIN in natural fats and oils. Palmitin has the formula

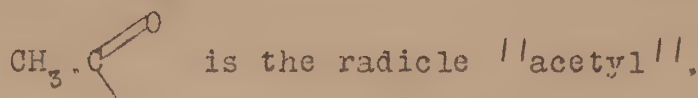
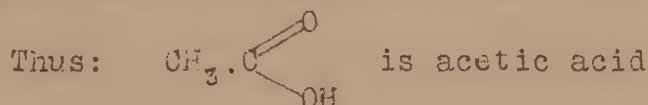


STEARIC ACID, $\text{C}_{17}\text{H}_{35}\text{COOH}$, occurs as glyceryl stearate, or STEARIN in the natural fats.

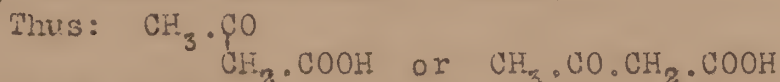


OLEIC ACID, $\text{C}_{17}\text{H}_{33}\text{COOH}$, corresponds to the ethylene hydrocarbon $\text{C}_{17}\text{H}_{34}$. As OLEIN, or glyceryl oleate it occurs with stearin and palmitin in fats and oils.

ACETO-ACETIC, OR DIACETIC, ACID; or the ethyl ester of the same are occasional urine constituents. In order to understand the constitution of these bodies it must be understood that if the hydroxyl group be taken from the carboxyl group of an organic acid, the residue (or acid radicle) can still enter into combinations.



If we will replace one of the hydrogen atoms in acetic acid by acetyl, we obtain aceto-acetic acid.



It will be seen from the above formula for aceto-acetic acid, that it is both a ketone and an acid. Aceto-acetic acid and acids which, like it, contain a $=\text{CO}$ group, are often termed KETONIC ACIDS.

Ethyl Aceto-acetate has the formula: $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}.\text{C}_2\text{H}_5$.

(N.B.: These notes give no important practical points with respect to any compound mentioned — provided that compound is practically treated in the literature furnished in the courses in physiological and pathological chemistry. With respect to such compounds, the purpose here is to fix their position and relations in a systematic organic chemistry. The student will therefore continually compare these notes with his own notes of the lectures; with the set of notes on pathological chemistry; and with Halliburton's 'Essentials of Chemical Physiology.')

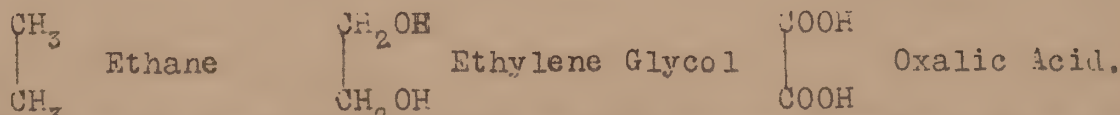
LACTIC ACID, $\text{CH}_3.\text{CHOH}.\text{COOH}$, partakes of the nature of an alcohol and of an acid. When carbohydrates ferment in the presence of decay-ing nitrogenous compounds, lactic acid results. Therefore lactic acid occurs in sour milk. It is a thick syrupy liquid.

HYDRACRYLIC ACID is the name of the isomeric lactic acid, $\text{CH}_2\text{OH}.\text{CH}_2.\text{COOH}$.

OXALIC ACID, $\text{COOH}.\text{COOH}$, consists of two carboxyl groups linked together. Oxalic acid is the type of DIBASIC organic acids — just as sulphuric acid is the type of dibasic mineral acids. The following comparison between certain oxalates and sulphates will make clear the relation stated.

$\begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$ Oxalic Acid	$\begin{array}{c} \text{COOK} \\ \text{COOK} \end{array}$ Potassium Oxalate	$\begin{array}{c} \text{COOH} \\ \text{COOK} \end{array}$ Acid Potassium Oxalate.	$\begin{array}{c} \text{COO} \\ \text{COO} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{Ca}$ Calcium Oxalate.
$\begin{array}{c} \text{H} \\ \diagup \\ \text{SO}_4 \\ \diagdown \\ \text{H} \end{array}$ Sulphuric Acid	$\begin{array}{c} \text{K} \\ \diagup \\ \text{SO}_4 \\ \diagdown \\ \text{K} \end{array}$ Potassium Sulphate	$\begin{array}{c} \text{H} \\ \diagup \\ \text{SO}_4 \\ \diagdown \\ \text{K} \end{array}$ Acid Potassium Sulphate	$\text{SO}_4 = \text{Ca}$ Calcium Sulphate.

Certain calculi consist chiefly of calcium oxalate. Sodium oxalate is produced on a large scale by fusing saw dust with sodium hydroxide. From sodium oxalate thus prepared the oxalic acid of commerce is obtained. Oxalic acid is a white crystalline body. The evolution and general relations of oxalic acid will be understood from an inspection of these formulae:



SUCCINIC ACID, $\text{COOH}.\text{CH}_2.\text{CH}_2.\text{COOH}$, which occurs in amber, is a derivative of butane.

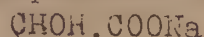
MALIC ACID, $\text{COOH}.\text{CH}_2.\text{CHOH}.\text{COOH}$, is closely related to succinic acid. It occurs in many plants and fruit juices — unripe apples, for instance. When pure is a deliquescent crystalline mass.

TARTARIC ACID, $\text{COOH}.\text{CHOH}.\text{CHOH}.\text{COOH}$, is one of the most important

of organic acids. Large quantities of acid potassium tartrate, or "cream of tartar" are obtained as a by-product in the wine industry.



"cream of tartar."



Rochelle Salt.



The "Seidlitz powder" reaction.

CITRIC ACID, $\begin{array}{c} \text{CH}_2.\text{COOH} \\ | \\ \text{COH.COOH} \\ | \\ \text{CH}_2.\text{COOH} \end{array}$, occurs in many vegetable structures;

but particularly in lemons. It crystallizes in large prisms; and is the most important of the TRIBASIC organic acids — being thus analogous to orthophosphoric acid among mineral bodies.

PROMINENT ESTERS NOT PREVIOUSLY MENTIONED.

The esters may be generally prepared by the action of acids upon the alcohols.

ETHYL ACETATE, $\text{CH}_3.\text{COO.C}_2\text{H}_5$, occurs in wines and wine vinegar. It is a colorless, volatile and very fragrant liquid.

ETHYL NITRITE, $\text{C}_2\text{H}_5.\text{NO}_2$, is the essential constituent of "sweet spirit of nitre". When pure it is a colorless, very fragrant liquid. It decomposes very readily and its solutions deteriorate so rapidly that they should not be kept long without tests being made to ascertain their strength.

ETHYL CHLORIDE, $\text{C}_2\text{H}_5.\text{Cl}$, or "sweet spirit of salt" is gaseous at ordinary temperatures. Its solution in alcohol has been used in medicine.

ETHYLIDENE CHLORIDE, $\text{CH}_3.\text{CHCl}_2$.

ETHYL BROMIDE, $\text{C}_2\text{H}_5.\text{Br}$.

AMYL ACETATE, $\text{CH}_3.\text{COO.C}_5\text{H}_{11}$.

AMYL NITRITE, $\text{C}_5\text{H}_{11}.\text{NO}_2$.

GLYCERYL NITRATE, $\begin{array}{c} \text{CH}_2.\text{NO}_3 \\ | \\ \text{CH}.\text{NO}_3 \\ | \\ \text{CH}_2.\text{NO}_3 \end{array}$, otherwise called NITROGLYCERINE,

is the essential explosive constituent of dynamite. Also used in medicine. Obtained by the action of nitric acid on glycerine. Colorless, sweet tasting, oily liquid.

CELLULOSE NITRATES. One of the proofs of the alcoholic character of cellulose is its ability to form nitric acid esters. Cellulose, when acted upon by nitric acid, readily forms three nitric acid esters — depending on the strength of the nitric acid used. Note the following:

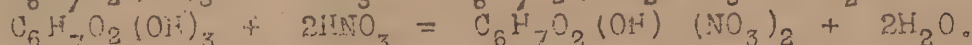


CELLULOSE, $(C_6H_{10}O_5)_n$ CELLULOSE MONONITRATE, $C_6H_9O_4(NO_3)_n$ CELLULOSE DINITRATE, $C_6H_8O_3(NO_3)_2_n$ CELLULOSE TRINITRATE, $C_6H_7O_2(NO_3)_3_n$

Cellulose dinitrate is soluble in a mixture of alcohol and ether, the solution being the familiar COLLODION solution. The dinitrate when incorporated with camphor forms the useful substance known as CELLULOID.

Cellulose trinitrate is commonly called GUN COTTON. It is an important explosive. Can be exploded wet or dry.

The formation of the cellulose nitrates may be expressed thus:



THE ETHERS.

The esters are often spoken of as "ethers", but the true ethers bear the same relations to metallic oxides, as the alcohols bear to the metallic hydroxides, or as the esters bear to the metallic salts.

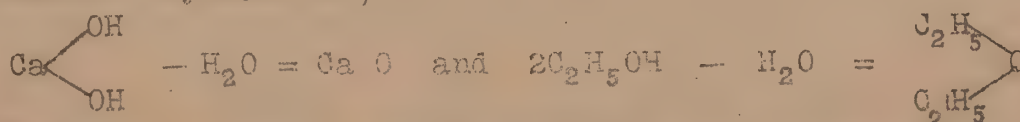
These statements will be understood after an inspection of the following comparisons:—

METALLIC OXIDES	ETHERS	METALLIC HYDROXIDES	ALCOHOLS	METALLIC SALTS	ESTERS.
$\begin{array}{c} K \diagup O \\ K \diagdown \end{array}$ Potassium Oxide	$\begin{array}{c} C_2H_5 \diagup O \\ C_2H_5 \diagdown \end{array}$ Ethyl ether	$\begin{array}{c} KOH \\ \text{Potassium} \\ \text{Hydroxide} \end{array}$	$\begin{array}{c} C_2H_5OH \\ \text{Ethyl} \\ \text{Alcohol} \end{array}$	$\begin{array}{c} K \diagup SO_4 \\ K \diagdown \end{array}$ Potassium Sulphate	$\begin{array}{c} C_2H_5 \diagup SO_4 \\ C_2H_5 \diagdown \end{array}$ Ethyl sulphate
$\begin{array}{c} Ca=O \\ \text{Calcium} \\ \text{Oxide} \end{array}$	$\begin{array}{c} CH_2 \diagup O \\ CH_2 \diagdown \end{array}$ Ethylene Oxide.	$\begin{array}{c} Ca \diagup OH \\ Ca \diagdown OH \\ \text{Calcium} \\ \text{Hydroxide} \end{array}$	$\begin{array}{c} CH_2OH \\ CH_2OH \\ \text{Ethylene} \\ \text{Glycol} \end{array}$	$\begin{array}{c} Ca \diagup NO_3 \\ Ca \diagdown NO_3 \\ \text{Calcium} \\ \text{Nitrate} \end{array}$	$\begin{array}{c} CH_2.NO_3 \\ CH_2.NO_3 \\ \text{Ethylene} \\ \text{Nitrate.} \end{array}$

ETHYL ETHER, $\begin{array}{c} C_2H_5 \diagup O \\ C_2H_5 \diagdown \end{array}$, or ETHYL OXIDE, is common ETHER. Ethyl

ether is the only ether we need to mention. Its mode of formation from alcohols is entirely analogous to the formation of metallic oxides from metallic hydroxides,

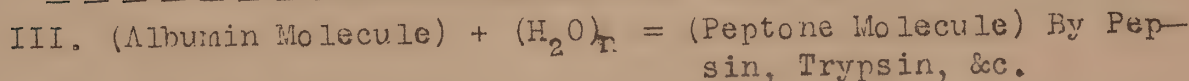
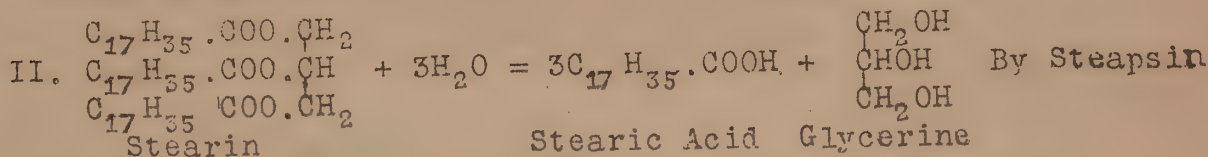
Thus



The dehydration of ethyl alcohol in the process of manufacture of ether is accomplished by the action of boiling dilute sulphuric acid (hence the term "sulphuric ether" sometimes applied to ethyl oxide)

$$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{SO}_4 \\ \diagup \\ \text{H} \end{array} + \text{C}_2\text{H}_5\text{OH} = \begin{array}{c} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{O} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} + \text{H}_2\text{SO}_4$$

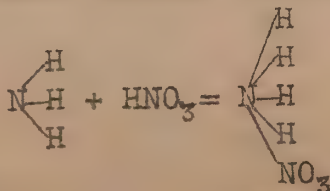
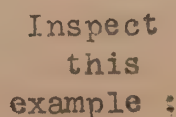
EXAMPLES:



THE AMINES. (AMMONIA DERIVATIVES).

ALKALOIDS.

While the alcohol radicles — like methyl, $-\text{CH}_3$; ethyl, $-\text{C}_2\text{H}_5$; propyl, $-\text{C}_3\text{H}_7$; ethylene, $=\text{C}_2\text{H}_4$; glyceryl, $\equiv\text{C}_3\text{H}_5$; &c. — have, in their compounds, decided analogies to the metals, the analogies are mainly analogies of position in molecular structures only. The metals are commonly strongly basic in character; while the alcohol radicles have but slight basic tendency. Now in the group of atoms NH_3 we have a most strongly basic compound. NH_3 combines directly with acids to form true salts. When NH_3 combines with acids to form salts, the previously trivalent nitrogen atom becomes pentavalent.



[illegible]

basic carbon compounds to which we have just alluded

...and

UNIT () would contain the same

IMD compounds contain the ammonia residue =NH .

as been said above the alleloids are exceedingly rare

ALL INFORMATION CONTAINED HEREIN IS UNCLASSIFIED

3. U.S. - TWENTY ALPHABETICALLY - BUT NOT IN DICTIONARY ORDER BY ALPHABET

25
15

RECEIVED BY AIR MAIL

312

52. 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94 96 98 100

3

2 4 2 2 4

$$\begin{array}{c}
 \text{C}_2\text{H}_4 \\
 \diagup \quad \diagdown \\
 \text{N} \quad \text{C}_2\text{H}_4 \quad \text{N} \\
 \diagdown \quad \diagup \\
 \text{C}_2\text{H}_4
 \end{array}$$
 is TRIETHYLENE DIAMINE. &c.

[illegible]

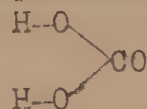
... may be considered as resulting either from the war

These may be considered as resulting either from the replacement

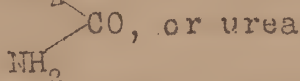
of hydrogen of ammonia by acid radicles (See page 30); or by the replacement of hydrogen directly united to carbon in the organic acids by the amido group ($-\text{NH}_2$). Some of these bodies are of greatest physiological importance. We will here study a few prominent examples.

UREA

Carbonic acid, H_2CO_3 may be written



From this acid we could have the radicle $=\text{CO}$. The amido derivative of this radicle would be NH_2



Pure urea consists of long, easily soluble, colorless crystals, that taste like saltpetre. Urea is the chief end product of the metabolism of nitrogenous substances in the human animal.

$(\text{CON}_2\text{H}_4)\text{HNO}_3$ is UREA NITRATE.

$(\text{CON}_2\text{H}_4)\text{HCl}$ is UREA HYDROCHLORATE

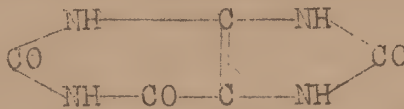
GLYCOCOLL or AMIDO ACETIC ACID has the formula, $\text{CH}_2\text{NH}_2\text{COOH}$. It is related to HIPPURIC ACID, the chief end product of nitrogen metabolism in the herbivorae.

Hippuric acid has the formula, $\text{C}_6\text{H}_5\text{CO}$ and is a derivative of CH_2COOH benzene and benzoic acid, as well as a derivative of glycocoll.

LEUCINE is a crystalline body that occurs in the pancreas and in various animal juices, and among the products obtained by boiling albuminous bodies with alkalis or acids; or by putrefaction. Leucine is amido-caproic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

URIC ACID, which is the chief end product of nitrogen metabolism in birds and reptiles, is related to urea.

Uric acid has the formula



Uric acid is a remarkably insoluble body. So are the ordinary urates hence the tendency of these bodies to form calculi. Uric acid is a weakly dibasic acid. The ordinary salts of uric acid are the acid salts. Acid lithium urate is one of the most soluble of the urates--hence the use of lithium compounds to dissolve calculi.

URIC ACID, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$.

ACID POTASSIUM URATE, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3\text{.K}$

ACID SODIUM URATE, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3\text{.Na}$.

ACID AMMONIUM URATE, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3\text{.NH}_4$

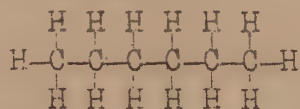
ACID LITHIUM URATE, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3\text{.Li}$

GUANINE (from guano), XANTHINE (in calculi, urine &c.)

THEOBROMINE (in cocoa), and CAFFEINE OR THEINE (in tea and coffee) are closely related to uric acid.

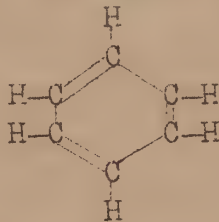
-- AROMATIC COMPOUNDS. --

All of the compounds that we have so far considered have been classed under the general term "The Aliphatic Compounds". This grouping under the one term is made because of their chemical correlation with each other as derivatives of the hydrocarbon methane, CH_4 . If, however, we examine their structural formulae, it will be seen that they might very properly be termed, "The Open Chain Series of Carbon Compounds" — the term alluding to the chain like linkage between the carbon atoms of the respective molecules. Take for example the hydrocarbon, normal hexane



The "open chain" of linked carbon atoms is striking.

Now the term "open chain" would have but little significance, and be merely a curious fact, were it not that there is another very large class of carbon compounds that have a mutual chemical relation with each other and the molecules of which contain nuclei consisting of closed chains of carbon atoms. This large group of carbon compounds may be considered as derived from benzene, C_6H_6 . All known facts point to the following as the probably correct structural formula for benzene:



It cannot be as directly affirmed that the molecule of benzene has the above structure, as it has been that methane and its derivatives have the structure we have assigned them. But by assuming the above structure for benzene, practically all pertinent known facts are explained by, and are in harmony with it. Following Kekulé¹, the great originator of this system, chemists have adopted the structure as correct.

The benzene or aromatic series of carbon compounds are so termed because of their relation to benzene as a parent body; and because they are common constituents of aromatic oils and resins.

The derivatives of benzene are obtained by replacing one or more of its hydrogen atoms by other atoms or atomic groups. It is to be noted that the "closed chain" of six carbon atoms — the benzene nucleus — is torn apart with great difficulty.

GENERAL STATEMENTS CONCERNING THE DERIVATIVES OF BENZENE.

The more important derivatives of benzene are those obtained by replacing one or more of the hydrogen atoms of benzene by the follow-

ing radical groups. $-\text{NO}_2$; $-\text{SO}_3\text{H}$; $-\text{OH}$; $-\text{C}_n\text{H}_{2n+1}$ (i.e. alkyl groups, such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$ &c.) $-\text{NH}_2$; $-\text{N}=\text{N}-$; &c.

NITRO COMPOUNDS.

By acting on benzene or benzene derivatives with nitric acid, one or more of the original benzene hydrogen atoms is replaced by the group $-\text{NO}_2$. (The number of $-\text{NO}_2$ groups introduced into the molecule being dependent on the nature of the aromatic body under treatment; on the strength of the nitric acid used: &c.) The compounds thus obtained are termed NITRO COMPOUNDS. This reaction is characteristic of the benzene derivatives.

Examples of Nitro derivatives of aromatic compounds:—

Proximate parent bodies.	C_6H_6 Benzene	$\text{C}_6\text{H}_5.\text{NO}_2$ is Nitro-benzene. $\text{C}_6\text{H}_4.(\text{NO}_2)_2$ is Dinitro-benzene. $\text{C}_6\text{H}_3.(\text{NO}_2)_3$ is Trinitro-benzene.
	$\text{C}_6\text{H}_5\text{OH}$ Phenol	$\text{C}_6\text{H}_5\text{OH} . (\text{NO}_2)_3$ is Trinitro-phenol or Picric acid.

AMIDO COMPOUNDS.

By reducing the nitro compounds with nascent hydrogen the group $-\text{NO}_2$ is finally changed to the group $-\text{NH}_2$. The compounds that contain this $-\text{NH}_2$ group are termed AMIDO-COMPOUNDS.

AZO and DIAZO COMPOUNDS.

These compounds stand intermediate between the nitro and the amido compounds. They contain the group $-\text{N}=\text{N}-$.

Examples of diazo-, azo-, and amido- derivatives of aromatic compounds:—

Proximate parent bodies.	$\text{C}_6\text{H}_5.\text{NO}_2$ Nitro-benzene	$\text{C}_6\text{H}_5.\text{NH}_2$ is Amido-benzene or Aniline. $\text{C}_6\text{H}_5.\text{N}=\text{N}-\text{NO}_3$ is Diazo-benzene Nitrate.
	$\text{C}_6\text{H}_4(\text{CH}_3).\text{NO}_2$ Nitro-toluene	$\text{C}_6\text{H}_5.\text{N}=\text{N}.\text{C}_6\text{H}_5$ is Azo-benzene. $\text{C}_6\text{H}_4(\text{CH}_3).\text{NH}_2$ is Amido-toluene or Tolidine.

SULPHONIC ACIDS.

The action of sulphuric acid on members of the aromatic series of compounds is to produce a replacement of one or more (according to conditions — see nitro-compounds) of the original benzene hydrogen atoms by an equal number of $-\text{SO}_3\text{H}$ groups. The resulting compounds are termed sulphonic acids.

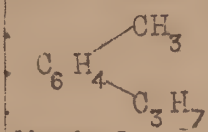
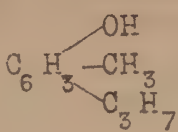
Examples of Sulphonic acids:--

Proximate parent body.	C_6H_6 Benzene	$C_6H_5.SO_3H$ is Benzene sulphonic acid.
	C_6H_5OH Phenol.	$C_6H_5(OH).SO_3H$ is Phenol sulphonic acid.

PHENOLS.

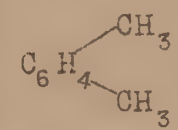
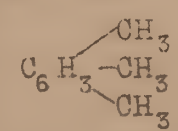
The group $-OH$ may be made to take the place of hydrogen atoms in aromatic compounds. The resulting compounds are phenols.

Examples of phenols:--

Proximate parent body.	C_6H_6 Benzene	C_6H_5OH is Oxybenzene or Phenol.
		$C_6H_3:(OH)_3$ is Trioxybenzene or Pyrogalllic Acid.
	 Methyl propyl benzene.	 is Methyl-propyl phenol or Thymol.

ALKYL DERIVATIVES.

These arise from a replacement of hydrogen atoms in benzene by those radicals of the aliphatic series that have been designated "alkyls". The alkyl groups thus introduced are termed "side chains". Examples of alkyl derivatives of benzene.

C_6H_6 Benzene	$C_6H_5.CH_3$	is Methyl benzene or Toluene.
		is Dimethyl benzene or Xylene.
		is Trimethyl benzene or Mesitylene.

ALCOHOLS OF THE AROMATIC SERIES.

When hydrogen atoms in the "side chains" are replaced by $-OH$, the alcohols of the aromatic series result.

These "aromatic" alcohols behave on oxidation like the "fatty"

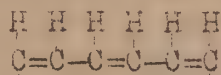
alcohols. That is, the primary alcohol groups change to the aldehyde and acid groups; and the secondary alcohol groups change to the ketone group. We thus have the "aromatic" ALDEHYDES, ACIDS and KETONES. Examples of aromatic alcohols, aldehydes, acids and ketones:—

Proximate	$C_6H_5.CH_3$ Toluene	$C_6H_5.CH_2OH$ is Benzyl Alcohol.
		Oxidation products of benzyl alcohol.
parent		$C_6H_5.CHO$ is Benzaldehyde. $C_6H_5.COOH$ is Benzoic acid.
body.	$C_6H_5.C_2H_5$ Ethyl benzene	$C_6H_5.CHOH.CH_3$ is Phenyl methyl carbinol. Oxidation of above. $C_6H_5.CO.CH_3$ is Phenyl methyl ketone.

ISOMERISM AMONG THE BENZENE DERIVATIVES.

We have already referred to Kekule's view of the structure of the benzene molecule (C_6H_6). This view is, in short, that the six carbon atoms are joined together in a "closed-chain" by alternating single and double unions, each carbon atom being also joined to one hydrogen atom.

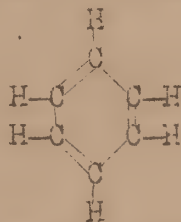
This view could be represented as below:



This view gives a perfectly structural symmetry.

For each hydrogen atom is linked to a carbon atom, which is in turn linked to one carbon atom by a single bond, and to another carbon atom by a double bond. Like atoms have therefore exactly similar methods of linkage and hence the structural symmetry.

Because of the structural symmetry of the benzene molecule, chemists are in the habit of writing it thus:



in the form of a hexagon. Furthermore, in order to conveniently simplify matters, the molecule is usually represented by a simple hexagon thus:

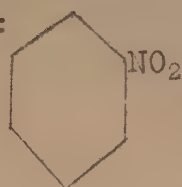


means Benzene, C_6H_6 .

When any of the hydrogen atoms are replaced by other atoms or groups, the resulting compound is readily represented structurally by

writing the respective symbols at the angles where replacements have occurred.

Examples:



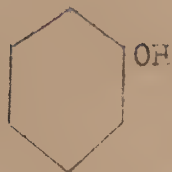
means $C_6H_5.NO_2$
or Nitro-
benzene.



means $C_6H_5.NH_2$, or
Amido-benzene or
Aniline.



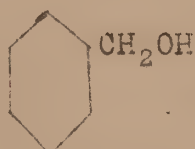
means $C_6H_5.SO_3H$, or Benzene
sulphonic acid.



means $C_6H_5.OH$, or Phenol
or Carboic Acid.



means $C_6H_5.CH_3$ or
Methyl Benzene or
Toluene.



means $C_6H_5.CH_2OH$, or Benzyl Alcohol.

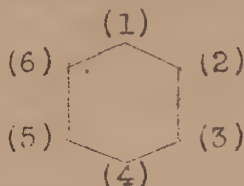


means $C_6H_5.CHO$, or Benzaldehyde.



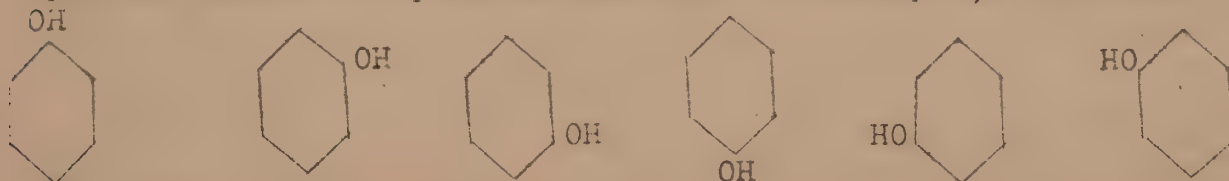
means $C_6H_5.COOH$, or Benzoic Acid.

The several angles may be understood to be numbered from one to six.



The utility of this numbering will appear in what follows.

It is obvious from the symmetry of benzene that when only one of its hydrogen atoms is replaced by a certain monovalent atom or atomic group, the structure will be the same no matter which of the six hydrogen atoms is replaced. Therefore for example, the bodies

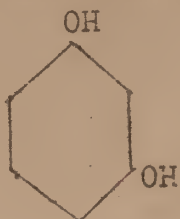
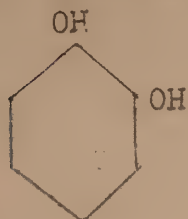


are structurally identical. As a matter of fact we find no isomeric bodies corresponding to the above substitution of a single atom of

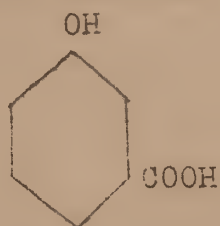
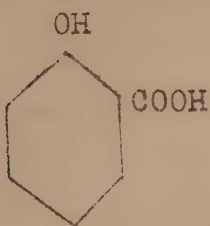
hydrogen in benzene by a certain group.

When MORE THAN ONE of the hydrogen atoms of benzene are replaced by a certain group, structural differences may arise.

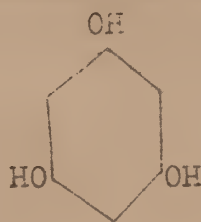
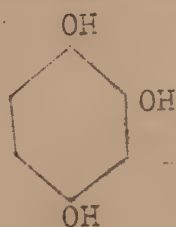
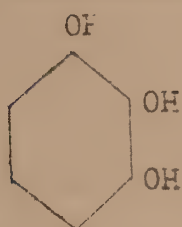
Thus we may have the following as possible structures:--



ACTUALLY EXIST AS
Pyrocatechin,
Resorcin,
Hydrochinon.

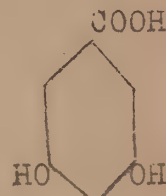
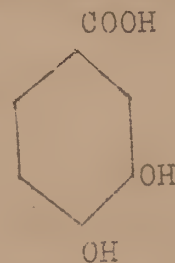
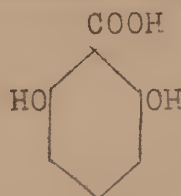
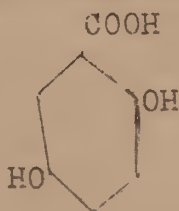
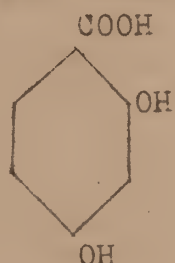
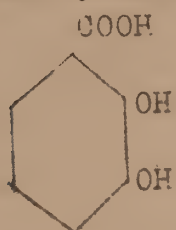


ACTUALLY EXIST AS
Salicylic Acid,
Oxybenzoic Acid.
Paraoxybenzoic Acid.

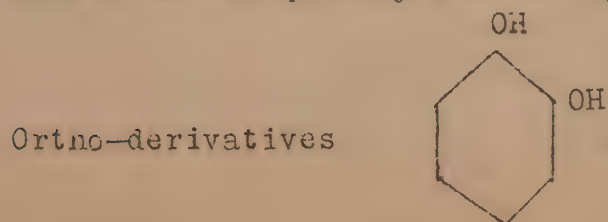


ACTUALLY EXIST AS
Pyrogallic acid
Oxyhydrochinon
Phloroglucin.

There are six possible structures corresponding to the general formula $C_6H_3(OH)_2.COOH$; and all of these six DIOXYBENZOIC ACIDS have been obtained and identified. The structures are given below:--

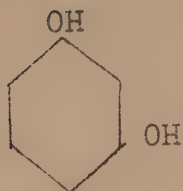


In the above manners arise the isomerism peculiar to the derivatives of benzene. By supposing each angle of the hexagon to have its number we can quickly and easily designate any of the various bodies.



is most simply written $C_6H_4(OH)_2(1,2)$

Meta-derivatives



is most simply written $C_6H_4(OH)_2(1,3)$

Para-derivatives



is most simply written $C_6H_4(OH)_2(1,4)$

From the above discussion it has become apparent that we may have three isomeric disubstituted benzenes corresponding to one of the following general formulae, in which x and y refer to any monovalent atom or atomic groups.



When the two substituting atoms or atomic groups occupy the (1,2) position, the compound is called an ORTHO-compound.

When the two substituting atoms or atomic groups occupy the (1,3) position, the compound is called a META-compound.

When the two substituting atoms or atomic groups occupy the (1,4) position, the compound is called a PARA-compound.

Examples illustrating the above nomenclature:—

$C_6H_4Cl_2$ (1,2) is Orthodichlorobenzene.

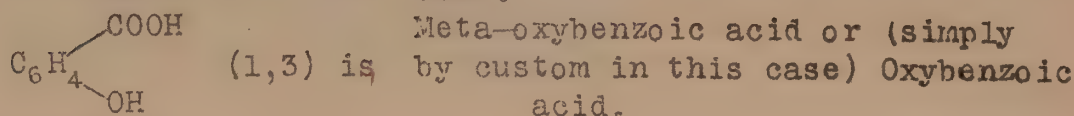
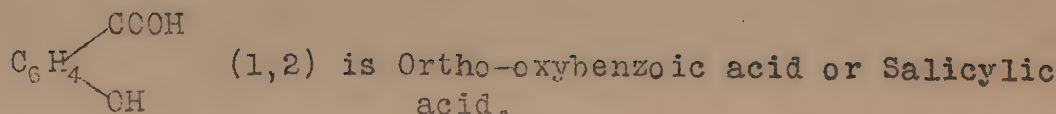
$C_6H_4Cl_2$ (1,3) is Metadichlorobenzene.

$C_6H_4Cl_2$ (1,4) is Paradichlorobenzene.

$C_6H_4:(NO_2)_2$ (1,2) is Ortho-dinitrobenzene.

$C_6H_4:(NO_2)_2$ (1,3) is Meta-dinitrobenzene.

$C_6H_4:(NO_2)_2$ (1,4) is Para-dinitrobenzene.



BENZENE AND ITS HOMOLOGOUS HYDROCARBONS.

These have the general formula $\text{C}_n\text{H}_{2n-6}$

Synthetically the benzene homologues are prepared by the indirect substitution of one or more of the hydrogen atoms of benzene by an equal number of alkyl groups. We may illustrate such syntheses by the following synthesis of toluene.



The benzene hydrocarbons are obtained almost exclusively from coal tar by fractional distillation. Physically they are, for the most part, volatile liquids. They find their chief application in the manufacture of aniline dyes. Among the benzene hydrocarbons are found numerous interesting examples of true isomers — Thus, we have four isomeric bodies corresponding to the formula C_8H_{10} , as follows:

$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ is Ethylbenzene.

$\text{C}_6\text{H}_4:(\text{CH}_3)_2$ (1,2) is Orthodimethylbenzene or Orthoxylene.

$\text{C}_6\text{H}_4:(\text{CH}_3)_2$ (1,3) is Metadimethylbenzene or Metaxylene.

$\text{C}_6\text{H}_4:(\text{CH}_3)_2$ (1,4) is Paradimethylbenzene or Paraxylene.

NITRO-DERIVATIVES.

The nitro-derivatives of the aromatic compounds are prepared by the direct action of nitric acid (more or less concentrated). By such treatment, one or more of the original benzene hydrogen atoms is replaced by an equal number of NO_2 groups.

NITROBENZENE, $\text{C}_6\text{H}_5\text{NO}_2$, is the most familiar of these nitro compounds — being known in commerce by the names "oil of mirbane" and "artificial almond oil", — this last name because of the odor. Nitrobenzene is a yellow liquid, largely employed in the manufacture of aniline. It is prepared by the action of nitric acid on benzene:



There are many other nitro-derivatives of the aromatic compounds.

AMIDO-DERIVATIVES.

As has already been stated the action of nascent hydrogen upon the nitro compounds, accomplishes a reduction to corresponding amido

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compounds.

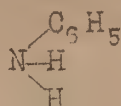
Thus (formation of aniline):—



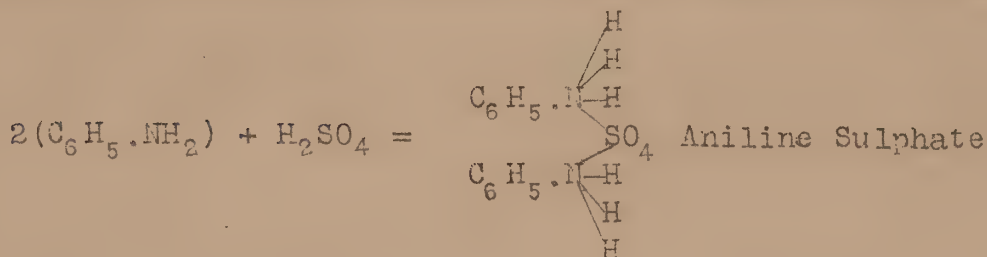
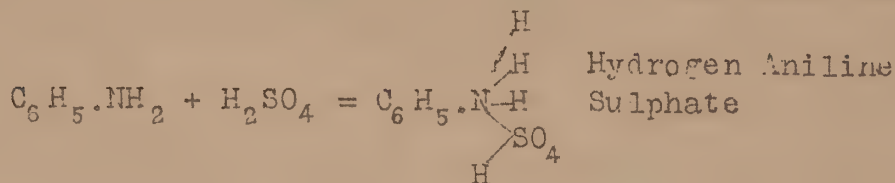
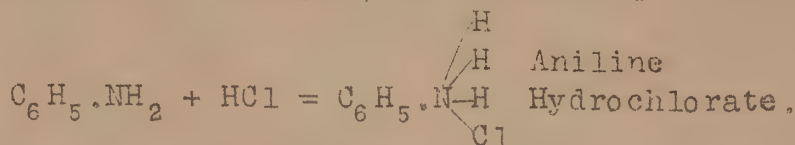
This reaction takes place in presence of free acid only.

ANILINE or AMIDOBENZENE is the simplest and most important of the aromatic amido compounds.

It is to be observed that aniline is also an amine, or ammonia derivative. To impress this fact we could write the formula



Like many amines, aniline is basic in its character; and forms salts with acids. We have, for example, the following aniline salts:



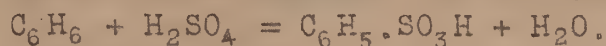
These examples of salts of aniline serve also to illustrate the general character of the salts of alkaloids belonging to the aromatic series of compounds.

The aniline dyes all of which are more or less closely related to aniline, are often extremely complicated in their structure. An example will be given under the head 'azo-compounds'.

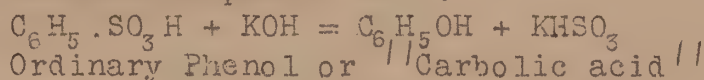
PHENOLS.

The phenols are HYDROXIDES OF AROMATIC RADICLES, in which one or more —OH groups have taken the place of an equal number of the original benzene hydrogen atoms. The phenols therefore contain one or more —O—H groups and are, so far, analogous to the tertiary alcohols of the aliphatic series of compounds. But they have rather a tendency toward an ACID character, than toward a BASIC character in their

chemical department; and are thus very different from alcohols. The phenols and their derivatives form a very important class of compounds. As has been stated previously, we may obtain sulphonic acids by the action of sulphuric acid upon aromatic compounds. If we further act upon the sulphonic acids with alkaline hydroxides, phenols result. For illustration of these facts consider the following reactions:—



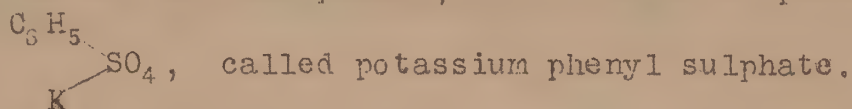
Benzene sulphonic acid.



Ordinary Phenol or Carbolic acid //

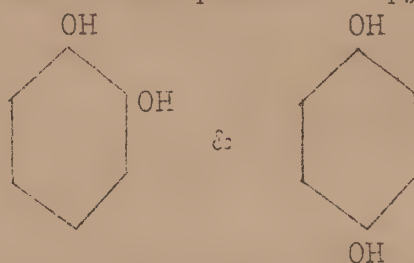
ORDINARY PHENOL, $\text{C}_6\text{H}_5.\text{OH}$ is also known as Carbolic Acid. It is when pure, a white crystalline body that melts readily, and is soluble in most ordinary solvents. Phenol is obtained from coal tar by distillation. Creasote, which is also obtained from tar, contains phenols.

Phenol occurs normally in the urine, sweat and faeces in small quantities, but especially after medical or surgical treatment with carbolic acid or other drugs containing a benzene nucleus. This occurrence of phenol is not of free phenol; but of combined phenol in the compound

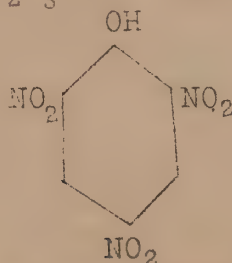


In the human body phenol is formed from proteids by the activity of enzymes and microorganisms in the intestine — hence its presence in the urine.

The dark color of the urine in //carboloria// is not due to carbolic acid, but to two other phenols — pyrocatechin and hydrochinon.

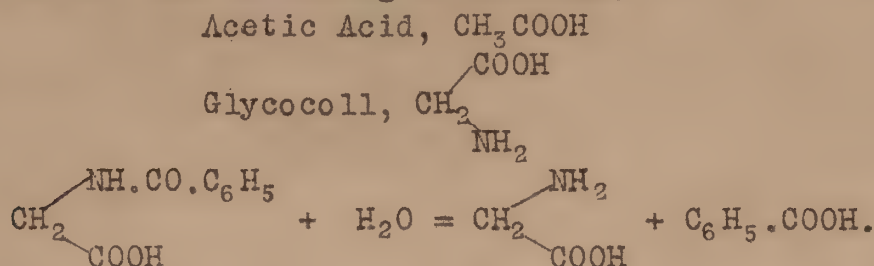


PICRIC ACID, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$. This body is trinitrophenol.



It consists of yellow crystalline plates. It is an important dye-stuff. With proteids it forms insoluble compounds. Hence its use to determine albumin in the urine.

HIPPURIC ACID, which occurs largely in the urine of herbivorous animals as a final product of the metabolic changes of proteid nitrogen, is related to benzoic acid and glycocoll. Glycocoll is amido-acetic acid. The constitution of hippuric acid will now be understood by an inspection of the following structures.



Hippuric Acid + water = glycocoll + benzoic acid.

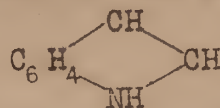
Hippuric acid is much less soluble than urea but more soluble than uric acid.

THE INDIGO GROUP.—

Compounds belonging to this group exist not only in plants but also in animals.

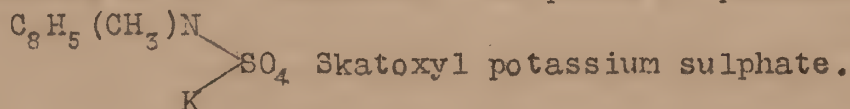
INDOL, $\text{C}_8\text{H}_7\text{N}$, is the simplest member of the group.

Structurally it has the formula



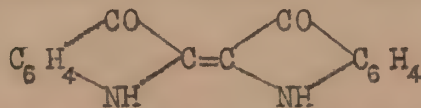
It is an oily fluid, having a peculiar odor. It is soluble in alcohol and ether and gives a red precipitate with nitric acid containing nitrous acid. Indol occurs among the decomposition products of proteids. Hence it is formed in the intestines. A portion of the indol thus formed is excreted with the faeces. The other portion, after absorption, finally passes into the urine as an ethereal sulphate. (See under skatol below.)

SKATOL, $\text{C}_9\text{H}_9\text{N}$. This body is METHYL INDOL, $\text{C}_8\text{H}_6(\text{CH}_3)\text{N}$. In combination, it is a well known constituent of the faeces and urine in which it occurs as an "ethereal" sulphate of potassium. Thus:



Like indol, skatol is a proteid decomposition product. Its absorption in large quantities during constipation is supposed to explain certain unpleasant symptoms. Skatol has a strong faecal odor.

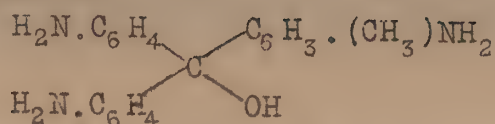
INDIGO BLUE. This important coloring matter has the formulae:



ROSANILINE.

Rosaniline will serve to illustrate the complex nature of certain of the "aniline" dyes.

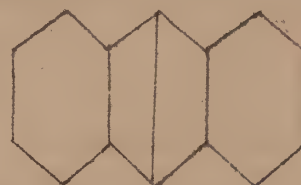
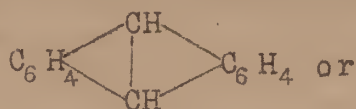
Rosaniline has the structure:—



Rosaniline may thus be regarded not only as a benzene derivative; but also as a derivative of methane.

ANTHRACENE GROUP.

ANTHRACENE, $\text{C}_{14}\text{H}_{10}$



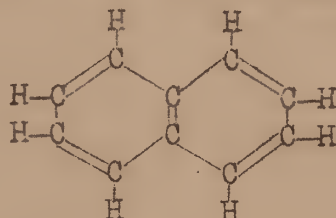
It must be understood that there are no hydrogen atoms at the re-entrant angles.

Anthracene is a solid constituent of coal tar. It is largely used in the preparation of dye-stuffs.

NAPHTHALENE GROUP.

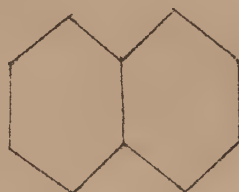
The parent body of this group is NAPHTHALENE, which consists of two benzene nuclei directly united with the elimination of two carbon and four hydrogen atoms. This is illustrated by the following structures:

The Naphthalene molecule.



C_{10}H_8

This may be expressed



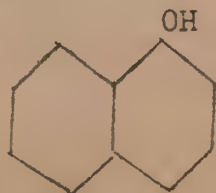
The reactions of naphthalene closely resemble those of benzene.

NAPHTHALENE, which is obtained from coal tar, has a peculiar odor and is a white, shining crystalline body much used as a basis for dyes. Its frequent use under the name of 'tar camphor' has made naphthalene a familiar body.

The phenol derivatives of naphthalene are important bodies; and are called 'naphthols'.

Examples are:

Alpha Naphthol



and Beta Naphthol



PHENANTHRENE

Like naphthalene this body is a "condensed" benzene:



Phenanthrene is a colorless, crystalline, body. Its solutions are fluorescent.

THE ALKALOIDS.

Among the derivatives of carbon, basic amines forms a very large group of compounds. These organic bases are called collectively, the alkaloids. The following genetic divisions of alkaloids are recognized

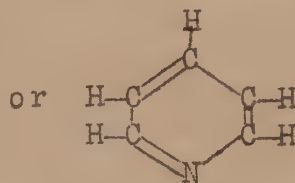
VEGETABLE ALKALOIDS:— Alkaloids obtained from plants.

ANIMAL ALKALOIDS:— Alkaloids obtained from animals.

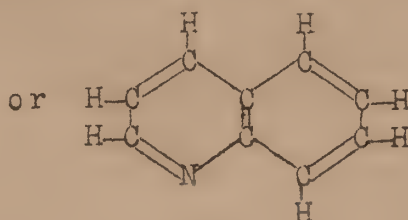
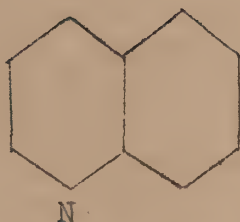
PTOMAINES:— Alkaloidal products of putrefaction.

LEUCOMAINES:— Alkaloidal products of animal metabolism.

Many of the alkaloids are comparatively simple amines. Others, again, are of exceeding complexity; and many such are related to the bodies pyridine and quinoline. The complete constitution of a large number of alkaloidal substances is unknown.



Pyridine.



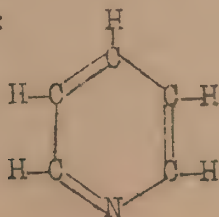
Quinoline.

EXAMPLES OF ALKALOIDS.

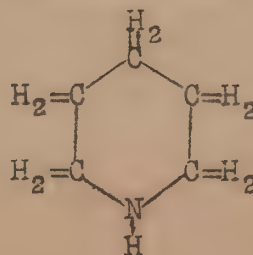
PIPERIDINE is the alkaloidal parent of piperine. Piperine occurs in pepper — hence the name.

Piperidine is Hexahydro-pyridine.

Thus:



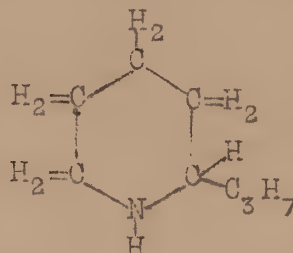
Pyridine.

Hexahydro-pyridine or
Piperidine.

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CONINE, the well known alkaloid from hemlock is alpha-normal propyl piperidine.

Thus:



NICOTINE, the essential alkaloid of tobacco has a still more complicated molecule, containing derivatives of two pyridine molecules. Nicotine is an oily, basic liquid, soluble in water. As a base, the nicotine molecule requires two molecules of a monobasic acid (like HCl) for saturation. This fact is in harmony with the presence in the molecule of TWO pyridine NITROGEN atoms.

MORPHINE, $C_{17}H_{19}NO_3 + H_2O$, is related to pyridine, quinoline and phenanthrene. Its exact constitution is unknown. Morphine hydrochlorate has the formula $C_{17}H_{19}NO_3 \cdot HCl + 4H_2O$. The water molecule, added to these formulae for morphine and its hydrochlorate occur as "water of crystallization". Morphine possesses remarkably strong reducing properties; and tests for morphine generally make use of this fact.

QUININE, which occurs to the extent of 2 or 3 parts per hundred in Calisaya bark, has the formula $C_{20}H_{24}N_2O_2$. Quinine is a diacid base related to quinoline.

STRYCHNINE, $C_{21}H_{22}N_2O_2$, is a monacid base related to quinoline and indol.

COCAINE, $C_{17}H_{21}NO_4$, is another important alkaloid related to pyridine.

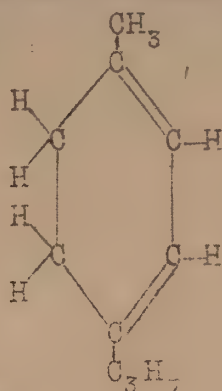
TERPENES.

The terpenes, constitute a very numerous; and but illy systematized group of hydrocarbons. The terpenes are chemically related to oil of turpentine; and are contained in the so called "volatile" and "etherical" oils. For the most part, the terpenes are obtained by distillation (with steam) of portions of plants belonging to the Coniferae and Citrus species.

General formula for terpenes, $C_{10}H_{16}$.

The terpenes are isomeric with the structure given below:

Dihydro-
para-methyl-
propyl-benzene.



EXAMPLES OF TERPENES

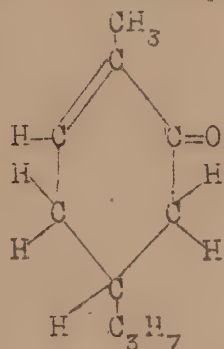
PINENE:— Is the chief ingredient of turpentine oil, of eucalyptus oil, juniper-berry oil, sage oil, &c.

CITRENE:— Characteristic of orange oil, lemon oil, cedar oil, dill oil and cumin oil.

IMPORTANT TERPENE DERIVATIVES — THE CAMPHORS.

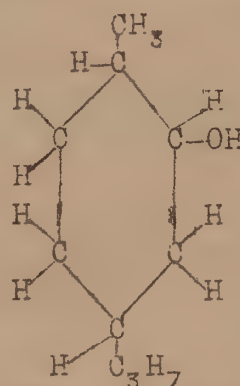
The peculiar-smelling substances called camphors, differ from the terpenes in containing oxygen; but are otherwise closely related to the terpenes. Two examples are given below:—

Ordinary
Camphor
(Japan)
 $C_{10}H_{16}O$



Mentha
Camphor

Menthol
 $C_{10}H_{20}O$



Oxy-hexa-
hydrocymene

IMPORTANT TERPENE DERIVATIVES— THE RESINS.

Like the camphors, the resins contain oxygen. They are closely related to the terpenes; and occur with the terpenes in plants. The natural thick solutions of resins in terpenes are called BALSAMS. The balsams upon exposure gradually become the vitreous solids called GUM RESINS, which latter are so largely used in the manufacture of VARNISHES.

The natural resins consist of more or less complex mixtures of peculiar aromatic acids, called the resin acids. Alkalis dissolve resins, with the formation of the so called resin soaps. The resin soaps are the soluble sodium or potassium salts of the resin acids.

Examples of typical gum resins are: Colophony, or common Rosin; Shellac; Amber and Gum Copal.

GLUCOSIDES.

Under the above term are conveniently included a large number of important carbon compounds, the chemistry of which is still but crudely defined. The classification has little to recommend it save convenience. All "glucosides", however, have this property in common. They are capable of splitting off a carbohydrate, when subjected to the action of hydrolytic agents (boiling dilute acid, ferments &c.). The carbohydrate thus produced is usually dextrose. The majority of glucosides are neutral bodies; but a few show an acid or basic nature.

A few well known glucosides are here mentioned:—

Amgdalin in kernels of fruit "stones"—splits up into Benzaldehyde, hydrocyanic acid and dextrose.

Carminic acid—Coloring matter of cochineal.

Digitalin—From foxglove.

Mucin—Compound of a proteid with a special carbohydrate called "animal gum".

Fermentation is the chemical changes in chemical systems

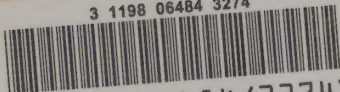
due to ferments.

A Ferment is a formless or morphologic substance that induces a chemical change in a chemical system and at the end of the reaction the system is permanently altered while the ferment remains unchanged.

Putrefaction: fermentation change taking place in Nitrogenous decomposition of Nitrogenous bodies by ferments

any substance that when acted on by hydro-lytic agents splits off a carbon.

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